

INVESTIGATION ON PROCESSES FOR REMOVAL OF CHLORAMINES FROM
SATURATED SODIUM CHLORIDE BRINE SOLUTION

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By

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ABSTRACT

ERCO Worldwide, a division of Superior Plus LP, Saskatoon facility ("ERCO Worldwide - Saskatoon") is a manufacturer of caustic soda, chlorine, hydrochloric acid and sodium chlorite. The brine solution as produced from the brine wells contains 26% sodium chloride. The saturated brine is purified and supplied to the electrolyzer system to produce caustic soda, chlorine, hydrochloric acid, and sodium chlorate. During the electrolysis of brine to produce sodium hypochlorite, chloramines are produced as undesirable products. These are chlorine contaminant which are detrimental to electrolysis process. Hence, it is essential to develop an efficient, and environmentally benign process to remove chloramines from brine. The objective of this project is to develop a suitable process to remove chloramines from brine. This project focuses on the evaluation of various processes available to remove chloramine from brine, test them in bench scale and recommend a process, which is adaptable with the existing ERCO operation. This study is divided into two phases: the first phase involves the application of ultraviolet radiation (UV) treatment to remove chloramines. The effects of solution pH (3-11), reaction time (15-45 min), concentrations of chloramines and ammonia to chlorine ratio (1:3 – 1:7) on chloramine removal were studied using the central composite design (CCD). Maximum chloramine removal of 100% was obtained at 30 mins reaction time, pH 3 and ammonia to chlorine ratio of 1:5. In the second phase, activated carbon (AC) was used for chloramines removal in an adsorption column. The influence of the mass dosage of AC (0.5 -1.5 g), flow rate (5-7 mL/min) and ammonia to chlorine ratio (4:20 – 7:35) on chloramine removal was studied. Maximum chloramines removal of 92% was observed at flow rate of 6 mL/min, 1 g AC dosage and ammonia to chlorine ratio of 1:5. Based on the results, UV treatment was found more effective in chloramine removal from synthetic solution.

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NOMENCLATURE

A variable	pH of solution
B variable	reaction time, (min)
C variable	ammonia to chlorine ratio
C_e	final ion concentration at equilibrium, (mg/L)
C_o	initial ion concentration at equilibrium
q_{max}	maximum adsorption capacity, (mg/mg)
M	mass of adsorbent, (g)
V	volume of solution, (mL)

ABBREVIATIONS

AC	Activated Carbon
BET	Brunauer, Emmett-Teller
CCD	Central composite design
DPD	N,N-diethyl-p-phenylene diamine
DC	Dichloramine
FT-IR	Fourier Transform Infrared Spectroscopy
FC	Free Chlorine
GAC	Granular activated carbon
MC	Monochloramine
PAC	Powdered Activated Carbon
TC	Trichloramine
UV	Ultra violet
XPS	X-Ray photoelectron spectroscopy
XRD	X-Ray Diffraction analysis

1. INTRODUCTION

ERCO Worldwide is a manufacturer of caustic soda, hydrogen, chlorine, sodium chlorate, and hydrochloric acid (see Figure 1.1). During the production process, saturated brine is purified and supplied to the electrolyzer system to produce caustic soda, chlorine, hydrochloric acid, and sodium chlorate. Brine is a solution consisting of sodium chloride (NaCl) and water. Chloramines are produced as undesirable products from the electrolysis of brine. The process water used for dissolving salt from underground salt mines also contains chloramines, which are ammonia derivatives formed by substitution of one, two or three hydrogen atoms with chlorine atoms. Thus, depends on the pH level of solution, 4.2, 8.5 and 9 will form monochloramines (MC), dichloramines (DC) and trichloramines (TC), respectively. Chloramines can be produced by the substitution of hydrogen on the amino groups with chlorine during chlorination. They are chlorine contaminants that could possibly influence the working operations of process vessels. Therefore, there is an urgent need to develop an efficient and cost effective process for chloramines removal. Thus, ERCO Worldwide requested University of Saskatchewan to find the solution for this problem. However, it is unknown whether chloramines removal challenges can be addressed by developing a process for removing chloramine from tap water which is an initial source of chloramines before injecting of it in brine caverns or develop a process of removal chloramines after injection of tap water, from brine.

Removing or reducing the concentration from process water alone, will not meet the requirements of ERCO Worldwide, based on the following reasons: if water with lower concentration of chloramine is supplied to the brine system, it will take more than 2.5 years for the improvements to occur in the brine quality. The holdup volume in brine caverns is approximately 900,000 m³ and all of this brine is contaminated with chloramine. As an example, if a suitable

process is to be developed to decrease the concentration in water from 0.4 ppm to 0.1 ppm and the treated water needs to be supplied to the brine system at the rate of 60 m³/h, it will take approximately 2.5 years for any improvements in brine to occur. This calculation is based on a well-mixed model. In practice, there is hardly any mixing in the brine wells, and therefore will take much longer for achieving any noticeable reduction in concentration.

If water is treated and supplied to the brine saturation process, immediate improvements to process operations in ERCO Worldwide cannot be achieved. However, if a process can be developed for reducing the concentration of chloramine from sodium chloride brine itself, the benefits are immediate. A number of reports are available on removal of ammonia and chlorine compounds from swimming pool and drinking water using activated carbon and UV technology (Xiao et al., 2009; Xue et al., 2017; Zhang et al., 2013; Jin et al., 2011; Kochany and Lipczynska-Kochany, 2008). However, limited data are available in literature on chloramine removal from city water using these technologies. Based on previous research on chloramine removal from water, it was found that granular activated carbon and UV technology can be used to reduce the concentration of chloramines in water (Keltsev, 1975; Bauer & Snoeyink, 1973; Lozada et al., 2018). Most of the data reported in literature using these two technologies are for quality of water at that particular site such as municipal wastewater treatment plant or swimming pool water, and likely, adapting suitable process is site specific. Data specific to the removal of chloramine from city water and brine needs to be studied to recommend a process for reducing chloramines concentration in Saskatoon city water and ERCO worldwide's brine solution. Also, ERCO brine data needs to be collected because contaminants present in brine might impact on the overall chloramine technology selection. Therefore, the aim of this research work is to establish important operating parameters for removal of chloramines from synthetic solution and brine using UV treatment, and

adsorption on activated carbons. In this research, experiments are performed using synthetic solution containing chloramines. The optimum operational conditions obtained with synthetic solution are then extended to examine, if it can be applied for treating sodium chloride brine.

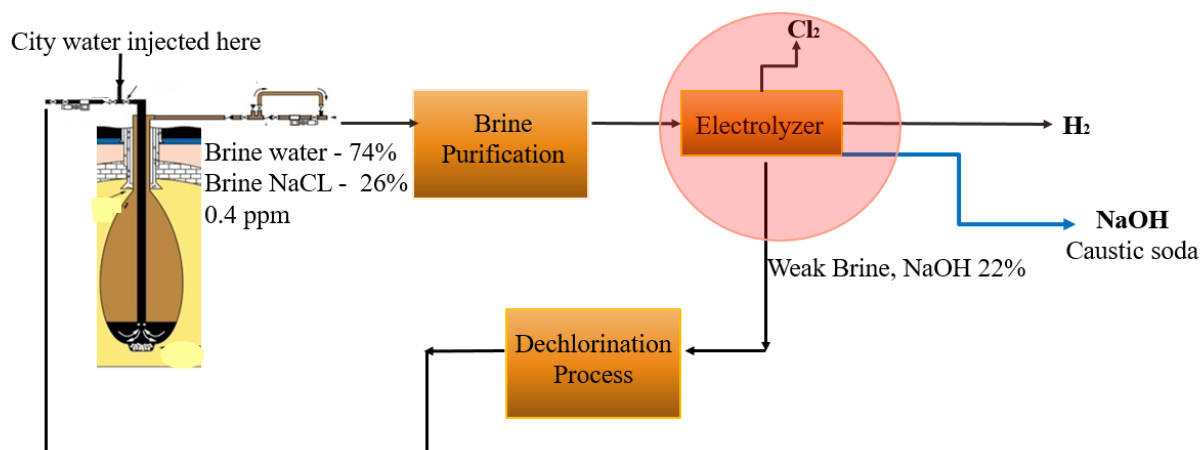


Figure 1.1 Schematic of current ERCO system

1.1 Knowledge Gaps

- No study has investigated the chloramines removal from brine solution using UV treatment processes.
- No study has investigated the chloramines removal from brine solution using adsorption by activated carbon.
- The comparison of the performances of these two technologies in terms of chloramine removal from brine solution is missing from the literature.

1.2. Hypothesis

- Based on the proven efficiency of UV processes for treatment swimming pool waters and other process waters, it is expected that UV treatment can be a successfully applied for chloramine removal from brine solution.
- Based on the proven efficiency of chloramines removal by adsorption on activated carbons from swimming pool and others process waters, this process is expected to be successful for chloramine removal from brine solution as well.
- The understanding of efficiency of different chloramines removal technologies will be helpful in the selection of the most effective technology for chloramine removal from brine solution.

1.3 Research objectives

Overall objective: To determine the best way of chloramine removal from brine solution due to its negative impact for process at ERCO Worldwide caustic soda production.

Specific objectives:

- Investigation of effects of UV treatment on chloramine removal from synthetic chloramine solution (prepared in laboratory by mixing ammonium chloride and sodium hypochlorite and named as synthetic solution) and real brine solution (obtained from ERCO worldwide and named as brine).
- Investigation of effects of activated carbon treatment on chloramine removal from synthetic chloramine solution and brine solution.

2. LITERATURE REVIEW

2.1. Chloramines

Chloramine became a popular disinfectant, even though it has a lower disinfection efficiency than free chlorine, because unlike free chlorine, it does not produce as much trihalomethanes (Komorita & Snoeyink, 1985). These chloramines have been studied due to their harmful respiratory effects on humans, particularly in the context of swimming pools (Barbot & Moulin, 2008). The formation of chloramines from ammonia and chlorine is discussed in detail in the following section.

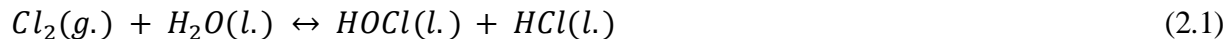
2.2 Chemistry of Chlorination

Chlorination is well established and mostly used in water treatment (Zhang et al., 2015). Chlorine is a member of halogen family and is denoted by the symbol Cl. It is highly reactive due to the presence of one unpaired electron in an outer valence shell. Elemental chlorine occurs as a two-atom molecule wherein each atom has 8 valence electrons in its outer shell and is represented by symbol Cl_2 , having a molecular weight of 70.92. This diatomic molecule is highly reactive as the bonding between the two atoms is relatively weak.

Ammonia (NH_3), is a compound made up of one nitrogen atom (atomic mass of 14) and three hydrogen atoms (atomic mass of 1) with a total molecular weight of 17.

All the three chloramine compounds resemble to molecular structure of ammonia. A chlorine atom will replace one, two, and three hydrogen atoms respectively for the formation of mono-, di-, and trichloramines.

Chlorine (Cl_2) is a gas that is heavier than air, toxic, and non-flammable, and is commonly used as an economically available oxidizing agent for disinfection. Chlorine for disinfection is available in one of three forms: calcium hypochlorite, sodium hypochlorite, and liquid chlorine. Compared to elemental chlorine as an oxidizing agent, the oxidizing effect of powdered calcium hypochlorite or aqueous sodium hypochlorite are the same. All three of them produce hypochlorous acid, which acts as an oxidizing agent for disinfection in water and wastewater. When chlorine gas is dissolved in water, it reacts with the water to form hypochlorous acid and hydrochloric acid (Equation 2.1):



Hypochlorite ion and hydroxide ion are formed on addition of hypochlorite to water



These forms can exist together and the relative concentrations of each depend on the pH of the solution, and not on the addition of chlorine gas or bleach.



The amount of chlorine added in either form is very small compared to the buffering power of most waters. The pH is therefore an important determinant of the proportions of hypochlorite ions and hypochlorous acid, as shown in Fig. 2.1. The activity of hypochlorous acid as a bactericide is almost 80% greater than that of the hypochlorite, and it is known that disinfection is less effective at higher pH values.

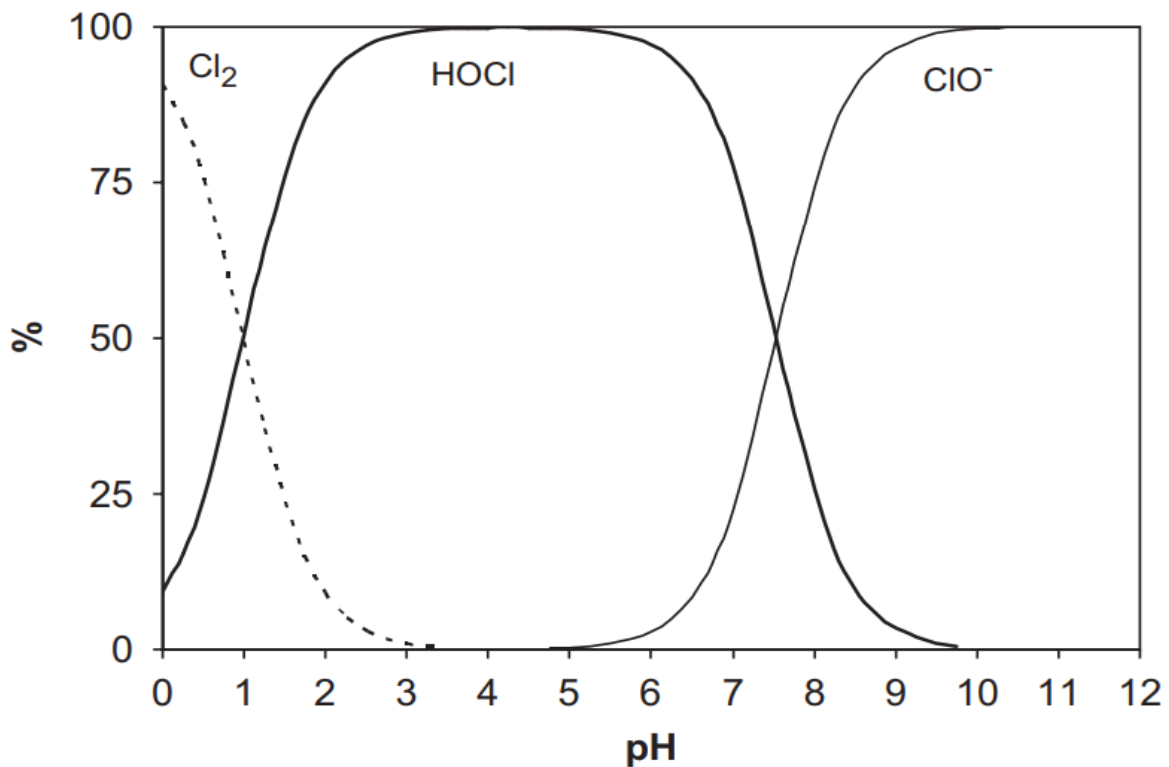


Figure 2.1 Equilibrium HOCl and OCl⁻ concentrations at varying pH (Deborde & von Gunten, 2008, reproduced with permission from the publisher, please see p. 73 in the Thesis)

All wastewater contains ammonia (NH₃) and chloramines are formed by reactions between hypochlorous acid. The reactions between HOCl and ammonia are as follows (equations 2.4-2.6):



These reactions are pH dependent occur instantaneously. Only monochloramine is formed above pH 8.5, a mixture of mono- and dichloramine forms below pH 8.5, and only nitrogen trichloride exists below pH 4.2 (Bauer & Snoeyink, 1973). The predominant species is monochloramine in ammonia and chlorine treated drinking or wastewater. Inorganic chloramines and ammonia can

interconvert by monochloramine disproportionation, substitution, and hydrolysis (Jafvert & Valentine, 1992; Vikesland et al., 1998, 2001). The reaction of the ammonia and hypochlorous acid will convert practically all of the free chlorine to monochloramine in less than one second at 25 °C and 5: 1 Cl₂ to NH₃ -N weight ratio (Berg, 1983).

Although these forms of chlorine are weaker than hypochlorous acid, they are very useful in some applications, but harmful in others.

2.3 Importance of monitoring

Scientist Berg (1983) recorded that during the production of monochloramines, careful monitoring of the chlorine to ammonia ratio ensures that chlorine is not underfed or overfed. Chlorine underfeeding can cause excess free ammonia to escape the facility (> 0.08 mg / L). Chlorine overfeeding can build the opportunity for the production of di-and trichloramine.

Chlorine overfeeding can establish the potential for the development of di-and trichloramine. Consistent free concentrations of 0.001 mg / L of ammonia from the plant will mean chlorine overfeeding.

2.4 Chloramine removal technologies

2.4.1 UV technology

According to Wang et al., (2016) research, Chlorination is well-developed technique and commonly used in water treatment process (as cited in Zhang et al., 2015). The chlorination could inhibit the micro-organisms growth and improve the quality of treated water. However, Kim et al., (2003) found that natural organic matter (NOM) and amino nitrogen in water sources can react with chlorine-based disinfectants to form chloramines and halogenated disinfection by-products

(DBPs) (as cited in Zhang et al., 2015). The formation of DBPs in waters can reduce the disinfectant efficacy of chlorination process. Alternative water treatment methods that are effective for both NOM removal and ammonia degradation may yield benefits. The UV/chlorine process has been considered as a novel water treatment method. Under UV/chlorine (UVC) irradiation, free chlorine photo-decomposes to form a chlorine radical ($\text{Cl}\cdot$) and hydroxyl radical ($\text{OH}\cdot$) as cited in Zhang et al., 2015). The result of UV/chlorine process depends on the wavelength(s) of the UV source, chlorine concentration as well as water quality. Another researcher found UV treatment effective for chloramine removal from water due to photodecomposition of NH_2Cl under UV irradiation, which leads to the formation of nitrate, nitrite without forming ammonia (Abdessemed, 2014).

2.4.2 UV technology parameters

EPA scientists (EPA, 2011) noted that damage from UV waves is primarily caused by wavelength irradiation within the spectrum UV-C region (200-280 nm) and is maximized at approximately 254 nm. This is the idea that disinfection uses UV treatment.

UV dose is usually expressed in mJ / cm^2 or J / m^2 units (where $1 \text{ mJ} / \text{cm}^2 = 10 \text{ J} / \text{m}^2$) and is a function of UV, mW / cm^2 and exposure time, s. Providers of patented UV disinfection systems market equipment are capable of administering a specified dose over a specified range of operating conditions (i.e. flow speed, water quality) and are certified for inactivation of bacteria, protozoan pathogens such as cryptosporidium, and viruses.

Zhang et al., 2015 discovered that the UV/chlorine system provides potential improvements over other treatment systems that already exists. The UV / chlorine cycle has been shown to be active in removing many pollutants, including methanol, chlorobenzoic acid,

trichloroethylene, and some emerging contaminants (Wang et al., 2016; Jin et al., 2011; Sichel et al., 2011; Zhang et al., 2013). An effective oxidation cycle for solar-driven UV / chlorine has also been reported (Chan et al., 2012). In addition, through several parallel pathways, the UV / chlorine cycle can inactivate waterborne microorganisms (Jin et al., 2011). The purpose of this research was to evaluate the effectiveness of the UV / chlorine system from two treatment goals: ammonia removal and DBP reduction.

2.4.3 Types of UV lamp technologies

There are three types of UV lamp: low pressure (LP), low pressure high output (LPHO) and medium pressure (MP). The typical properties of the various types of mercury lamps used in these systems are listed below in Table 2.1 (EPA, 2011).

Table 2.1 Typical properties of different UV lamp technologies

	LP	LPHO	MP
UV output range, nm	254	254	<200 to 600
Typical Power/lamp, W	40-85	100-500	1-30k
Efficiently. %	35	30	15
Warm-up time, min	2	5	10
Operating Temp., ° C	40	200	800
Lamp life	12, 000 hours (15 months)	12, 000 hours (15 months)	5,000 hours (7 month)
Power/Variability	No (on/off)	60% to 100%	30% to 100%

Compared to MP lamps, LP lamps Relative to MP lamps, LP lamps have lower power input and germicidal UV output, higher efficiency and longer life; but many more LP lamps than MP

lamps are required for a given dose, so MP plants are smaller for the same reason. LPHO lamp characteristics are intermediate between LP and MP.

As the age of mercury vapour lamps increases, their output decreases along with the depletion of the available mercury in the lamp through the quartz sleeve. The sizing of the UV disinfection system is typically based on the end-of-life UV dose (EOLL).

Aging factor is the measurement of a new lamp's output and a lamp's output at the validated life of the end of the lamp. Suppliers therefore require a fixed burn time before replacing lamps.

2.2.4 Advantages and disadvantages of UV disinfection

Downstream of UV disinfection is often observed a decrease in water chlorine production. The capital cost of UV disinfection systems is much lower than ozonation and membrane filtration and is roughly 1(UV): 5(ozonation): 10 (membranes) for medium to large installations. The operating costs of UV systems for medium to large installations are equally balanced.

Similarly the operating costs of UV systems for medium to large installations follow a corresponding cost ratio comparison of 1(UV): 3(ozonation): 8 membranes), (EPA, 2011).

Here are disadvantages of UV disinfection.

- UV disinfection does not leave any residue in treated water and therefore does not offer re-infection protection in the distribution pipework
- UV disinfection is not appropriate for use in treated surface water or groundwater supplies with an UVT (1 cm) of less than 75%, based on a detailed sampling history that involves seasonal variations in water quality.

- UV disinfection is only appropriate in decontamination of high-quality groundwater that does not require treatment or in decontamination of final process water that has reduced particulate matter, biological and chemical impurities after treatment.
- UV radiation does not affect the taste or smell if it happens in the water to be processed
- Nitrite formation from the UV reaction is the only potential by-product, formed by irradiation at wavelengths below 240 nm with nitrate in water, which can only pose a potential problem for MP systems, since LP and LPHO systems only transmit monochromatic UV light at 254 nm. However, proprietary MP systems generally include quartz sleeves that filter out the small portion of the UV spectrum at the lower frequency and thus eliminate the possibility of by-product formation in MP systems.

2.5 Activated carbon technology

Activated carbon is very effective adsorbent due to high surface area, pore volume and superior surface functionalities. Active carbons obtained from various types of solid raw material such as peat, anthracite, wooden material, leather industry waste, animal substances. Active carbon with high mechanical strength are made from coconut shells and other nuts, as well as from fruit pits. In the most developed industrial countries, active carbons is produced in large quantities and in a wide range. For example, in the United States, more than 90 grades of coal are produced, and the following decreasing series is analyzed in terms of consumption of the industry: purification of drinking and waste water, sugar refining, gas purification and vapor recycling, rubber production, medicines, lubricating oil purification, plastics production, purification of alcohol-aqueous solutions and wines. The annual production of active carbons in the United States is more than 70,000 tons. In 1965, in Japan, the consumption of powdered active black carbons was reached 15,000 tons and 2,000 tons for granulated. The main direction of the usage of powder

activated carbon in Japan is sugar refining. Also, in India activated carbon is received from different parts of tropical plants (Keltsev, 1976).

Activated carbon is mostly used in water treatment systems as filtration materials for their ability to adsorb a wide variety of charged water impurities. It has been demonstrated that activated carbon is not effective for the ammonia removal due its non-polar nature (Xue et al., 2017), but some studies have suggested that the removal of chloramines using activated carbon may be feasible (Barbot & Moulin, 2008; Stoquart, 2014). Many granular activated carbon filtration materials are commercially available.

2.5.1 Types of activated carbons

Based on the size and size, activated carbon can be divided into two types: (i) powdered activated carbon and (ii) granular activated carbon (Keltsev, 1976). Powdered activated carbons are produced with particle size of 0.15 mm. They are useful for purification of liquids.

Granulated activated carbons are usually produced in cylindrical shape with the diameter of 2-5 mm. Granulated activated carbons is used for purification of gas stream.

2.5.2 Chloramine Filters

Chloramine is a disinfectant used by many cities for city water treatment, thus chloramination an alternative to chlorination. However, chloramine is toxic and could negatively impact of human health. For this reason, the use of chloramine is restricted and an increasing number of scientists and health practitioners are concerned about ingesting even low levels of chlorine and chloramine in chlorinated or chloramine-treated water of showering / bathing (Barbot and Moulin, 2008).

The concern with chloramines is that conventional activated carbon filters do not kill them quickly as chlorine is. Calgon Carbon developed advanced catalytic carbon to reduce the contact time needed for successful extraction, making it a more practical alternative for treatment with chloramine. The ClearPlus™ Series Centaur Catalytic Carbon Filter specification is presented in Table 2.2.

On practice, granular activated carbon is wide used all over the world as an adsorbent for water filters. For instance, the company ClearPlus was developed a water filters with Calgon's catalytic granular activated carbon.

The essence of their ClearPlus™ Series Centaur Catalytic Carbon Filter systems, according to the manufacturer's exhortations, is their catalytic granular activated carbon (GAC) content. Activated carbon is highly effective adsorbent with surface area more than 3,000 m², widely known around the world.

Table 2.2 ClearPlus™ Series Centaur Catalytic Carbon Filter Specification

Control Valve:	Fleck 5800 SXT
Inlet/Outlet Connections:	1" MNPT
Operating Temperature:	36F to 100F (2 to 38C)
Operating Pressure:	20 to 90 psi (1.4 to 6.2 bar)
Replacement Media:	<u>Calgon® Centaur</u>
Typical Media Life:	5 Years

The effectiveness of activated carbon is determined by the size of the carbon granules, the carbon source, activated carbon purity, method of preparation and method of application.

Therefore, the application of activated carbon varies depending on its quality and purpose of its application.

The removal of chloramines can be greatly enhanced by the design of highly selective catalytically activated carbon. Calgon's Centaur catalytic granular activated carbon (GAC) is a bituminous carbon based coal developed after exhibit catalytic functionality for more suitable chloramine elimination yet hydrogen sulphide (H_2S) removal. The elimination over contaminants by granular activated coal happens namely an end result on catalytic reduction, adsorption yet mechanical filtration (retrieved from <http://www.home-water-purifiers-and-filters.com>).

Catalytic reduction-the chloramine bonds between chlorine and ammonia are broken when in contact with catalytically activated carbon and chlorine is reduced catalytically to harmless chloride ions. This method is very quick and does not use the surface of activated carbon, thus allowing it to be free to remove other pollutants and allow a very long filter life.

Adsorption - organic contaminants that cause bad taste and odors, along with most chemical contaminants, are adsorbed onto the media surface as a result of an electro-chemical attraction. Activated carbon has a large surface area for adsorption, as described above.

Mechanical Filtration-particles, dust and debris are physically removed from the water because they cannot pass between the granules through the gaps.

2.5.3 Filters with powdered activated carbon

Powdered activated carbon has been commonly used for the removal of organic compounds, including pesticides, insecticides and organic solvents (Humbert et al., 2008).

2.5.4 Granular activated carbon adsorption

Granular activated carbon (GAC) adsorption devices are commonly used in the treatment of drinking water. These systems consist essentially of stationary beds where the liquid flows through the adsorbent (GAC). At the top of the bed, adsorbed material accumulates first and then through the bottom of the bed. The maximum amount of contaminant that can be adsorbed into activated carbon occurs when the material is adsorbed.

In his study, Symons et al. (1981) used GAC as an adsorbent for chloroform and trihalomethanes extraction. He noticed that chloroform concentration had been decreased for three weeks by 90 percent or more, at which point the effluent chloroform concentration rose steadily until it was equal to the 10th week influent concentration. Bromine-containing trihalomethane was adsorbed more effectively

2.5.5 Combined chlorine removal from swimming pool water using activated carbon

An addition to environmental contaminants, other hazardous waste such as nitrogenous or carbonaceous compounds may be found in water in the bath. Nitrogenic compounds from urine and sweat may form chloramines in pools with HOCl, especially NH_2Cl and NCl_3 . Barbot and Moulin (2008) studied a hybrid treatment system (ultrafiltration/adsorption) that was installed between the buffer tank and the conventional treatment unit of a swimming pool. The pool water is already chlorinated and a dose of sodium hypochlorite (NaOCl) is added upstream in the treatment system. Before ultrafiltration, after ultrafiltration (before adsorption), after adsorption and on the pool surface, water samples were collected. The chlorine content was determined using diethylphenyldiamine (DPD) reaction samples and spectrophotometry concentration measurements. Effective chlorine was measured using a table relating effective concentration of chlorine to pH and free concentration of chlorine.

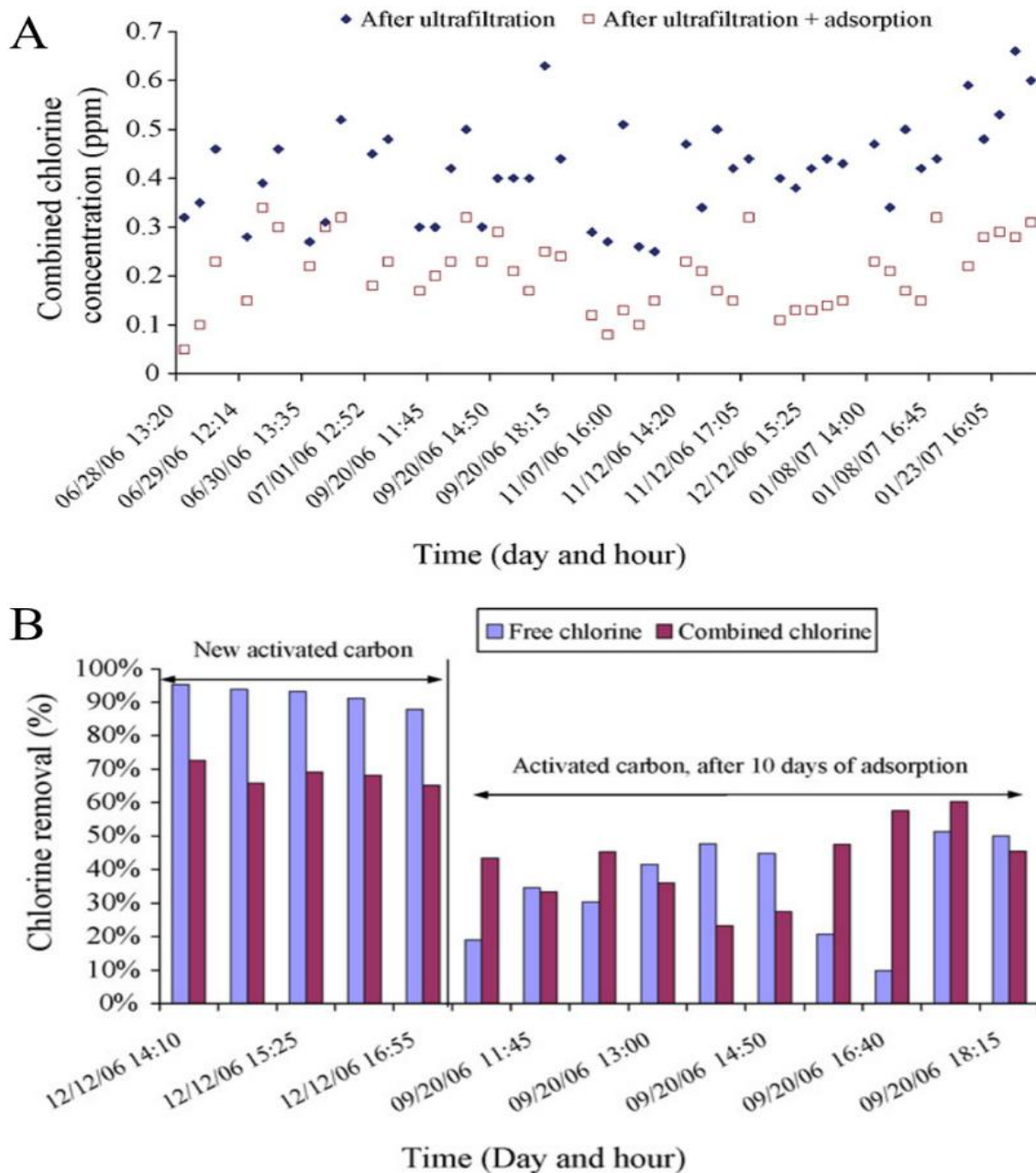


Figure 2.2 Combined chlorine concentrations before and after activated carbon adsorption (A) and free and combined chlorine removal percentages of fresh and 10-day-old Everzit SP® granular activate carbon (B) (Barbot & Moulin, 2008). (Reproduced with permission from the publisher, please see p. 77 in the Thesis)

Combined chlorine is measured as the maximum concentration of chlorine minus free concentration of chlorine. The method of adsorption was studied with respect to the combined removal of chlorine.

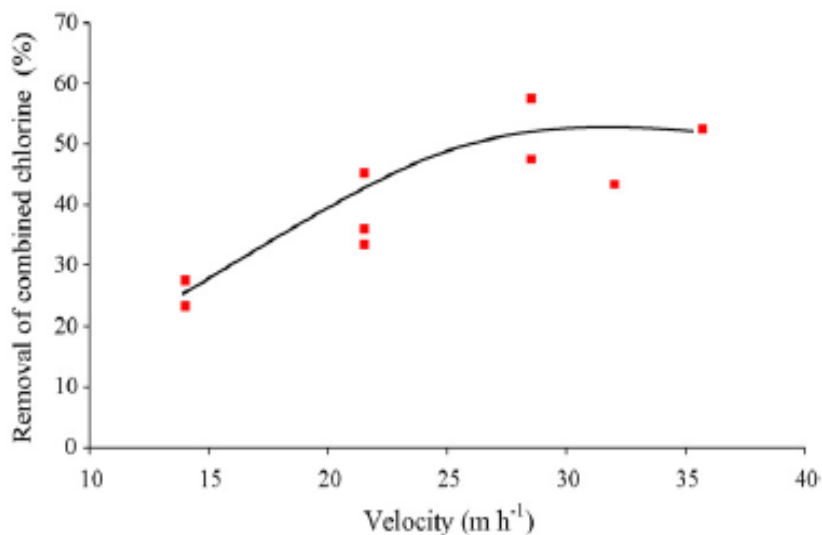


Figure 2.3 Effects of fluid velocity on the removal of combined chlorine by activated carbon adsorption (Barbot & Moulin, 2008) (Reproduced with permission from the publisher, please see p. 77 in the Thesis)

In terms of combined chlorine, the activated carbon chosen met the water quality requirements as the concentration after adsorption never reached 0.35 ppm (Fig. 2.2 A). The combined concentration of chlorine measured before and after ultrafiltration showed that the combined chlorine concentration after ultrafiltration (before adsorption) was higher due to the reaction, except shortly after backwashing.

Fig. 2.2 B shows the removal percentages across the adsorption units: separately for free chlorine and combined chlorine (including chloramines). The Fresh granular activated carbon in this study removed approximately 65% of combined chlorine. After 10 days, removal percentages generally decreased and varied more. These results were obtained specifically for initial combined

chlorine concentrations in the range of 0.3 to 0.65 ppm, which should be compared to the initial concentrations to be treated in industrial applications.

The authors also studied the influence of fluid velocity (between 10 and 35 m/h) in the adsorption unit on adsorption performance. The removal of combined chlorine increases with fluid velocity, and plateaus at around 30 m/h (Fig. 3.2).

The findings of this study related to the removal combined chlorine species, including chloramines, represent important considerations for selecting a chloramine removal strategy for industrial process water, along with the effect of fluid velocity. The implementation of activated carbon adsorption for chloramine removal from brine should consider the decrease in the chlorine removal percentages of the adsorption units after 10 days of operation, the initial chloramine concentrations to be treated, and the effect of flow velocity on removal efficiency.

2.5.6 Reactions of chloramines with activated carbon

The goal of the research by Bauer & Snoeyink (1973) was to study the modification of a chlorination process to reduce ammonia concentrations entering surface water. In their study, the authors highlighted that the incomplete oxidation of ammonia by chlorine leads to the formation of chloramines and they investigated the reaction of chloramines in active carbon. The incomplete oxidization of ammonia by chlorine (the formation of chloramines, as explained in the introduction above) may be advantageous because ammonia is difficult to remove by activated carbon adsorption. An activated carbon treatment following chlorination could therefore achieve a desirable ammonia concentration in the effluent. Controlling pH, which affects which chlorinated ammonia species are present in solution, is also important for controlling ammonia effluent concentrations. It was found that the concentrations of ammonia and chloramines was minimized at a pH of 6.4. In the chlorination process, gaseous chlorine was supplied at a controlled rate with a contact time of 15

min. Chlorination was followed by 10 min of contact with activated carbon in two expanded bed up-flow contactors (Bauer & Snoeyink, 1973).

This experiment was set up using coal-based activate carbon, and chloramine solutions were prepared using deionized water, free chlorine solutions, and a pH-7.4 buffer. The chloramine solution was stored in dark place for stabilization with room temperature. Chloramine concentration was measured by titration. Ammonia nitrogen was measured as a difference between the total N(-III) and combined nitrogen. The activated carbon treatment experiment was conducted directly in the sample bottles (suspended activated carbon treatment). More experimental details are provided in Bauer & Snoeyink (1973). The reaction with active carbon showed the immediate destruction of monochloramine. During the first 20 h of reaction with activated carbon, no increase in the concentrations of combined chlorine species was noted. Additional tests were designed to isolate the dichloramine reaction with active carbon. For those tests, a pH of 4.5 was used to isolate dichloramine. After 2 h of reaction between the dichloramine solution and the activated carbon, dichloramine was eliminated from the solution.

The tests showed that both monochloramine and dichloramine are removed by activated carbon treatment. The results of this study indicate that chlorine dosages below the breakpoint requirement can be used to oxidize ammonia if chlorination is followed by contact with active carbon. Without the usage of active carbon, dosages below the breakpoint result in large concentrations of total residual, including chloramines. In such cases, a post-treatment with activated carbon serves to destroy both combined and free chlorine residuals. Other studies have confirmed that using activated carbon following chlorination can reliably remove chloramines (Kochany & Lipczynska-Kochany, 2008).

2.5.7 Applicability of activated carbon treatment for the removal of chloramines from brine

From studies that have investigated the removal of chloramines and other combined chlorine species, it appears that chloramines can be reliably removed using activated carbon. However, important considerations include the age of the activated carbon and initial chlorination. Barbot & Moulin (2008) showed that combined chlorine removal percentages decrease with the aging of the activated carbon in a filtration/adsorption unit, and Bauer and Snoeyink (1973) showed that some chlorination is required to remove ammonia. This latter consideration could be beneficial in cases where chloramines are already formed. More research is needed to determine the feasibility of specifically removing chloramines from brine solutions using activated carbon, because activated carbon treatments rely on electrochemical interactions between aqueous species and the surfaces of the activated carbon. In brine solutions, there may be much more competition for the adsorption sites within the activated carbon.

2.6 Hypochlorite treatment

If sufficiently high dosages of chlorine are added to ammonia-containing waters, different reactions can occur resulting in ammonia destruction and free chlorine residual development. This is illustrated in the breakpoint curve for waters containing ammonia (Fig. 2.4). Low dosages of chlorine result in mono- and dichloramine production. The peak of the combined residual curve occurs when all free ammonia is used until chloramines are formed. When the chlorine dosage reaches 8

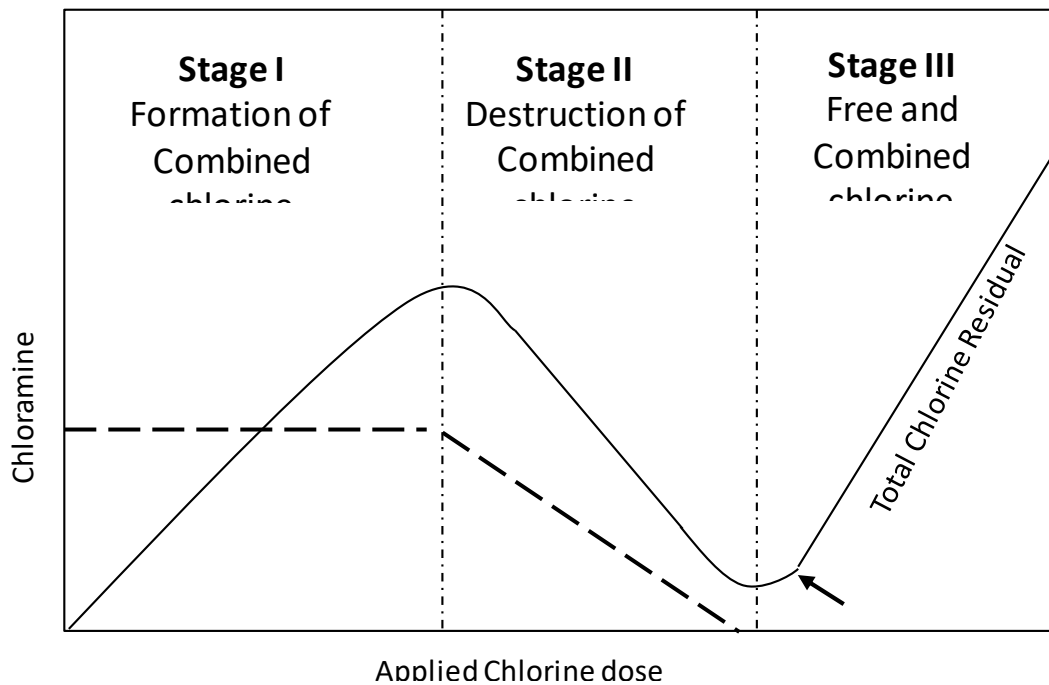


Figure 2.4 Ammonia Breakpoint Curve for Chlorination

or 10 times the ammonia concentration, the breakpoint is reached, after which the ammonia is destroyed and the free chlorine from the combined chloramines becomes present as a mixture of hypochlorous acid and hypochlorite at normal pH values.

Recognizing these two forms of residual chlorine is of great importance since the chemical, bactericidal and virucidal properties of free chlorine are vastly superior to those of chlorine combined in chloramines. In waters with excess chloramine, chlorination and promoting the formation of hypochlorite can therefore be used to reach the ammonia break point and remove chloramines. This chloramine removal technique is referred to as hypochlorite treatment.

2.6.1 Study on chlorination for chloramine removal

Due to its high efficiency, water disinfection from chloride electrolytic processing and hypochlorite is widely used in industry and no additional chemicals are required (Kraft et al., 1999). For the sum of chlorine, hypochloric acid and hypochlorite, the term active chlorine is used

in technical literature. A process called anodic oxidation, electrochemical disinfection, and electrochemical treatment is commonly used for disinfection for water treatment, and can also be used to hit the break point of ammonia and extract chloramine. Hypochlorite ion or hypochloric acid formed from the naturally occurring chloride ions in the processed water is the main disinfecting agent in this process. In electrolytic hypochlorite production there are two steps: the primary oxidation of chloride to chlorine at the anode surface and the subsequent formation of hypochlorite, equations 2.7 and 2.8.



Hypochlorous acid can dissociate to form hypochlorite and H^+ , the relative proportions of which depend on the pH of the water.

In a three-part study of electrolytic hypochlorite production (Kraft et al., 1999, 2002) ; all experiments used divided electrode compartments to prevent the reduction of produced hypochlorite at the cathode. Chloride solutions and a concentrated NaCl solution were prepared using deionized water. No supporting electrolyte was added. In the pH range of 6 to 9, the active chlorine is almost entirely hypochlorous acid and hypochlorite.

As shown in Figure 2.5, active chlorine production depends on the initial chloride ion concentration, the temperature of the water, and the current density of the electrodes. The active chlorine production rate on IrO_2 is always higher than that on platinum. For both electrode types, the active chlorine production rate increases with chloride concentration, decreases with temperature, and linearly increases with current and current density.

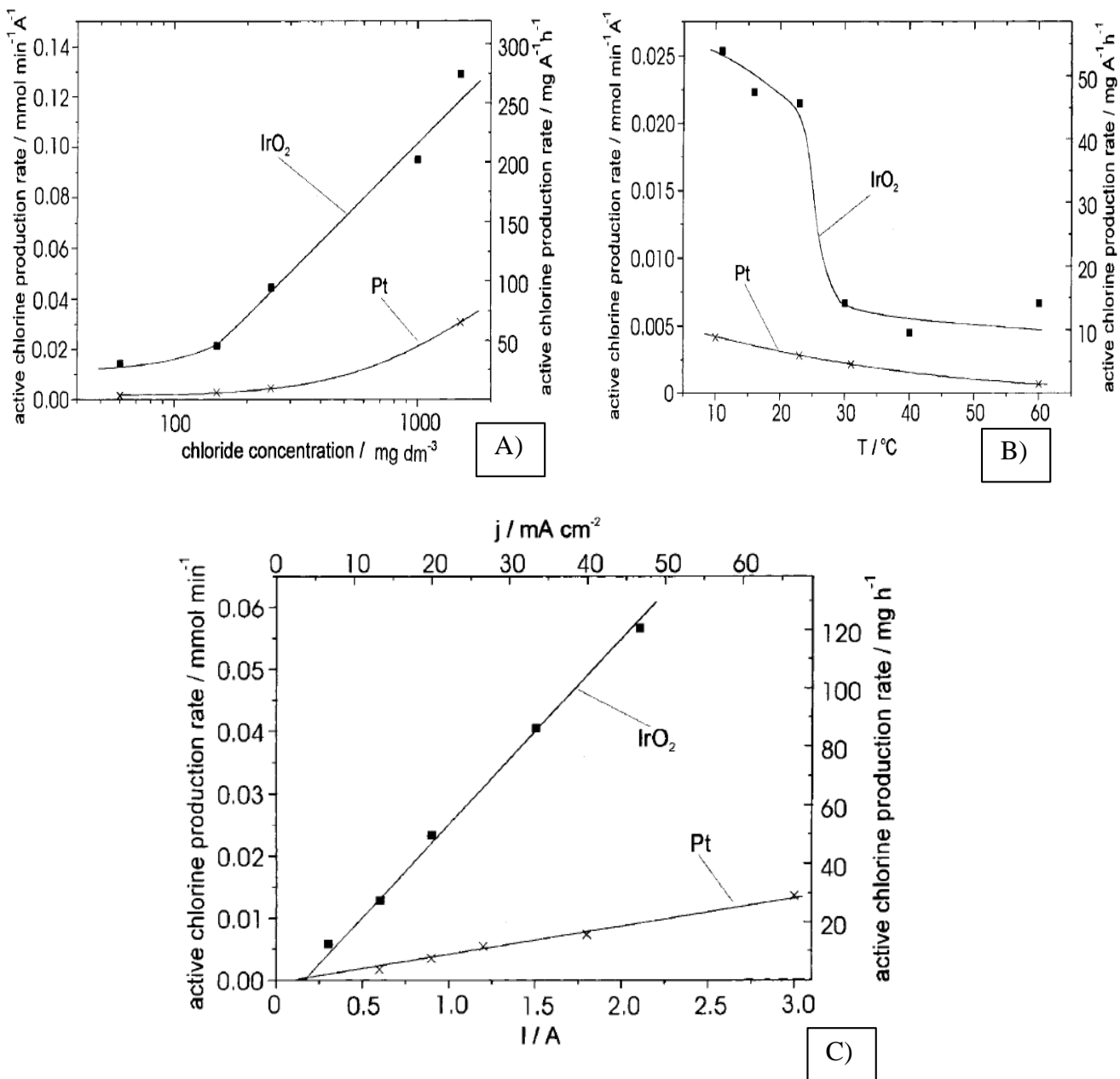


Figure 2.5 Active chlorine production rate using iridium oxide and platinum-coated titanium electrodes for (A) different initial chloride concentrations and current density of 15 mA cm⁻², (B) different temperatures for current density of 15 mA cm⁻², and (C) different current densities at temperature 23 °C for an initial chloride concentration of 150 mg dm⁻³ (Kraft, Stadelmann et al. 1999). (Reproduced with permission from the publisher, please see p. 75 in the Thesis)

2.6.2 Applicability of hypochlorite treatment for chloramine removal from brine

Before active chlorine can be formed to promote the removal of chloramines, the chloride demand of the water must be satisfied. The chlorination used to satisfy the chloride demand is usually termed breakpoint chlorination. This study by Kraft et al. (1999) was the first to demonstrate hypochlorite production in very dilute chloride solutions. For chloramine removal from industrial process waters, the parameters investigated by in that study will have to be considered differently. The electrolytic formation of active chlorine compounds could be enhanced by the high concentration of chloride ions in industrial brine solutions, but could also be hindered if the process water is hotter than room temperature. Of the electrode materials tested, iridium oxide electrodes consistently out-performed platinum electrodes for hypochlorite production. The observed linear increase in the active chlorine production rate with current density could be used to adjust the active chlorine production in line with changes in water quality, particularly in chlorine demand. Electrolytic hypochlorite production could be a promising option for removing chloramines from industrial brine solutions.

2.7 Study selection

There are only three ways might be applicable for chloramine removal from brine, however, hypochlorite treatment for chloramine removal from ERCO Worldwide brine was investigated earlier by Licudine et al. (2017). Thus, this research will consider UV technology and adsorption on activated carbon as a treatment for chloramine removal from saturated chlorine brine.

3. MATERIALS AND METHODS

3.1. Materials

All the reagents used in present study were of analytical grade. Phosphate buffer, sodium hypochlorite was procured from Sigma Aldrich Canada. Granular activated carbon (Centaur – C 12x40) was purchased from Calgon Carbon (Table 3.1). Millipore water was used in all the experiments.

Table 3.1 Characterization of granular activated carbon Centaur – C 12x40 by Calgon Carbon

Specification	Centaur - C 12x40
Iodine number, mg/g	900
Ash, wt%	5 (max)
Moisture (As Packaged), wt %	5 (max)
Density (Apparent), g/cc	0.5
12 US Mesh (1.7 mm), wt%	0.5
40 US Mesh (0.425 mm), wt%	4.0 (max)

3.2 Preparation of chloramine solutions

The preparation of chloramine solutions of different NH_4Cl to NaOCl ratios was performed by Kasaka et al. (2010).

NaOCl and NH_4Cl all were mixed and diluted with distilled water in different ammonia to chlorine ratios. After mixing for 30 min at 30°C , the standard NCl_3 solution was stored for about 1.5 h at 30°C and used for the experiments. The resultant solution was used for UV experiments.

According to Kasaka et al. (2010), different chloramine solutions were preparation, were prepared with different ammonia to chlorine ratio as shown in Table 3.2.

Table 3.2 Preparation of solutions with different NH_4Cl to NaOCl ratio

NH_4Cl to NaOCl ratio	NaOCl working solution volume (100 mM)	NH_4Cl working solution volume (100 mM)	Distilled water (mL)	Total volume (mL)
1:3	7.5	2.5	40	50
1:5	12.5	2.5	35	50
1:7	17.5	2.5	30	50

All components were mixed and diluted with distilled water. After mixing for 30 min at 30°C , the standard NCl_3 solution was stored for about 1.5 h at 30°C and used for the experiments. The resultant solution was used for UV experiments.

3.3 UV experiments procedure

The UV experiments were carried out using a 450-W medium pressure, quartz mercury-vapor lamp (ACE Glass Inc. 7861-245) (Fig. 3.1). As shown in Fig. 3.2, the UV irradiation reactor contains a glass reactor, a constant temperature water bath and a medium pressure Hg UV lamps is fixed in the center of the 1000 mL UV reactor.

In a typical experiment, 100 mL of chloramine sample placed in UV reactor and irradiated with UV light for desired time period (10 to 45 min). Throughout the reaction time, samples were

gently stirred with the use of a magnetic stirrer. After irradiation of the samples for pre-determined time intervals, residual concentrations of free chlorine (FC), monochloramine (MC), dichloramine (DC) and trichloramine (TC) were analyzed.

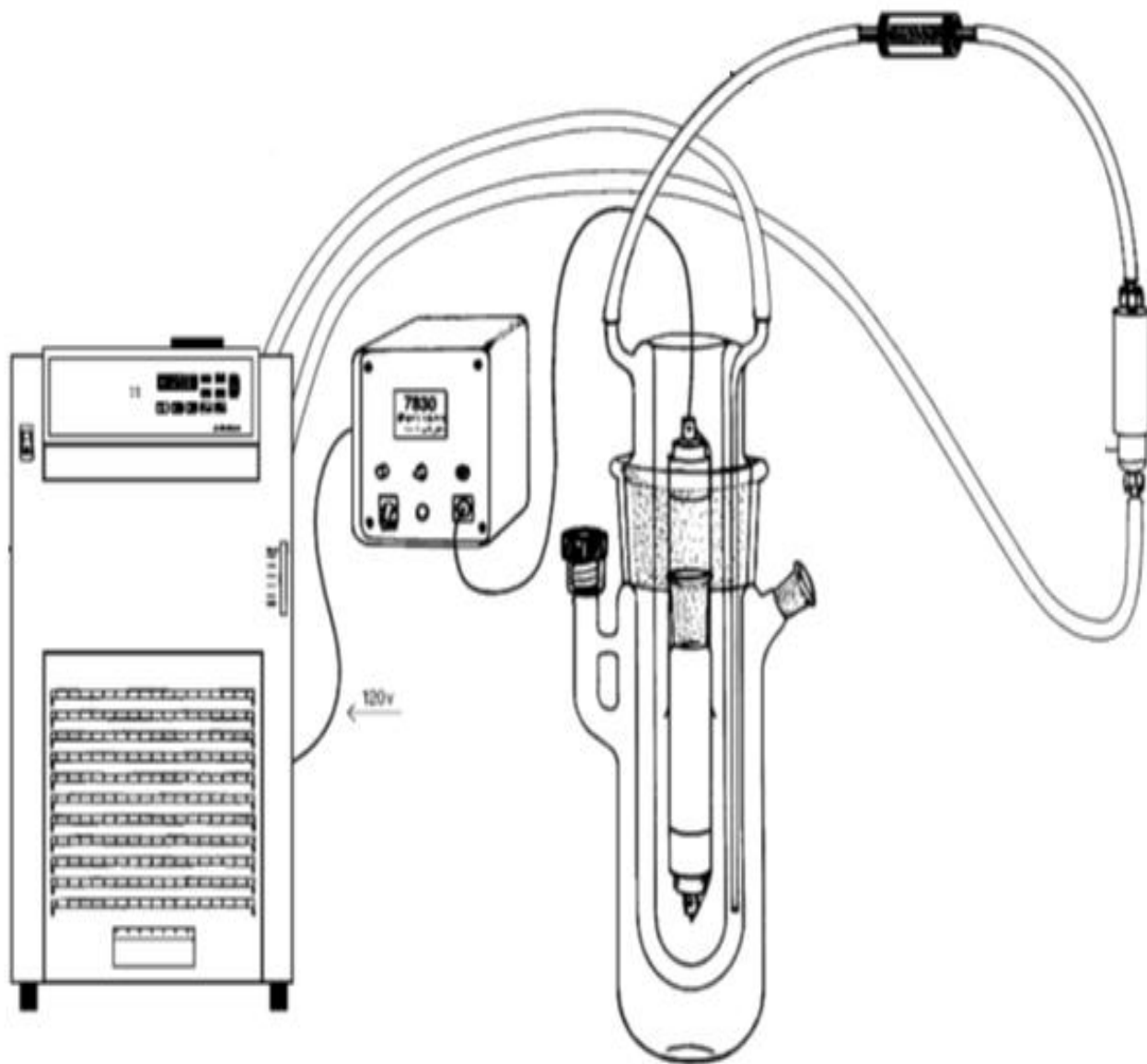


Figure 3.1 Schematic view of UV system (Supplied by ACE GLASS, Inc., Vineland, NJ, USA)

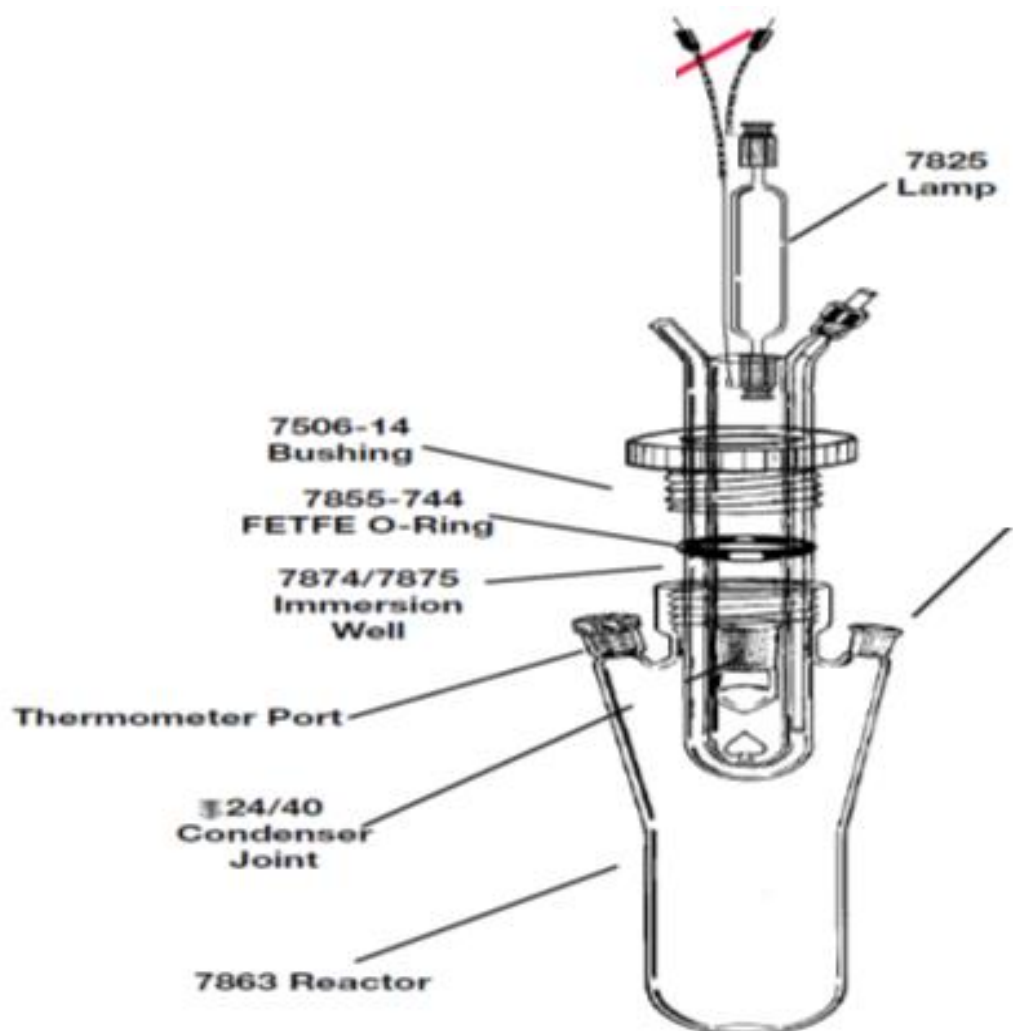


Figure 3.2 Schematic view of 450-W medium pressure quartz mercury UV reactor (Supplied by ACE GLASS, Inc., Vineland, NJ, USA)

3.3.1 Design of experiments

Central composite design (CCD) was applied for design of experiments and optimization of reaction parameters for removal of chloramines using UV system (Table 3.3). Three independent variables viz., A: Solution pH (3-11), B: reaction time (10 to 45 min) and C: NH_4Cl to NaOCl ratio (1:3 to 1:7) were considered for design the experiments. Combined chloramine concentration was assigned as the response factor.

Table 3.3 Design of experiments

Run no.	Solution pH (A)	Reaction time (min) (B)	Ammonia to chlorine ratio (C)
1	11	45	1:7
2	3	30	1:5
3	11	45	1:3
4	7	45	1:5
5	3	15	1:7
6	7	30	1:5
7	3	45	1:3
8	11	30	1:5
9	3	45	1:7
10	11	15	1:7
11	11	15	1:3
12	3	15	1:3
13	7	30	1:5
14	7	30	1:5
15	7	30	1:5
16	7	30	1:3
17	7	30	1:7
18	7	30	1:5
19	7	30	1:5
20	7	15	1:5

3.4 Procedure for adsorption on activated carbons

3.4.1 Batch experiments for an adsorption

For batch experiments, 50 mg of GAC was added to 150 ml conical flasks containing 50 ml of the solution. The pH of the solution was kept 5. The flask was then placed on incubation shaker and agitated at 120 rpm, at 25°C. All the experiments were done in duplicates. The samples were withdrawn after 24 h of reaction time and concentration of the chloramine was determined using UV-Vis spectrophotometer at 515 nm. The data obtained from the batch experiments was analyzed by adjustment to calibration curve equation and DPD calorimetric method of analysis. The maximum % removal were calculated from concentration values obtained, using following Equations 3.1 and 3.2:

$$q_{max} = \frac{(C_o - C_e)}{M} V \quad (3.1)$$

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3.2)$$

where, q_{max} (mg/g) is maximum adsorption capacity; C_o and C_e (mg/L) are the initial and final ion concentration at equilibrium; V (mL) is the volume of solution taken and M (mg) is the mass of adsorbent.

3.4.2 Adsorption column experiments

Adsorption column experiments on activated carbon were carried out in a glass column of 1.5 cm inner diameter and 70 cm height, containing a bed of granulated activated carbon (Fig. 3.3).

Glass wool packing is provided in the column to avoid the activated carbon loss during the operation and glass beads are used to support the bed. The setup is equipped with peristaltic pump

for circulation of chloramine solution from inlet tank to adsorption column. Chloramine solution of required concentrations was pumped upward through the activated carbon bed at required flow rate. The pH of the feed was measured continuously and maintained constant at pH ~ 6. Samples were collected at desired time intervals from top of the column and the residual concentration of chloramine in the effluent samples will be determined using UV- visible spectrophotometer. The effect of different operating parameters like flow rate, chloramine concentration and empty bed contact time (EBCT) on the chloramine removal rate was studied and different breakthrough conditions were then established from the data analysis. Breakthrough plots of C_t/C_i versus time will be obtained for different sets of column parameters.

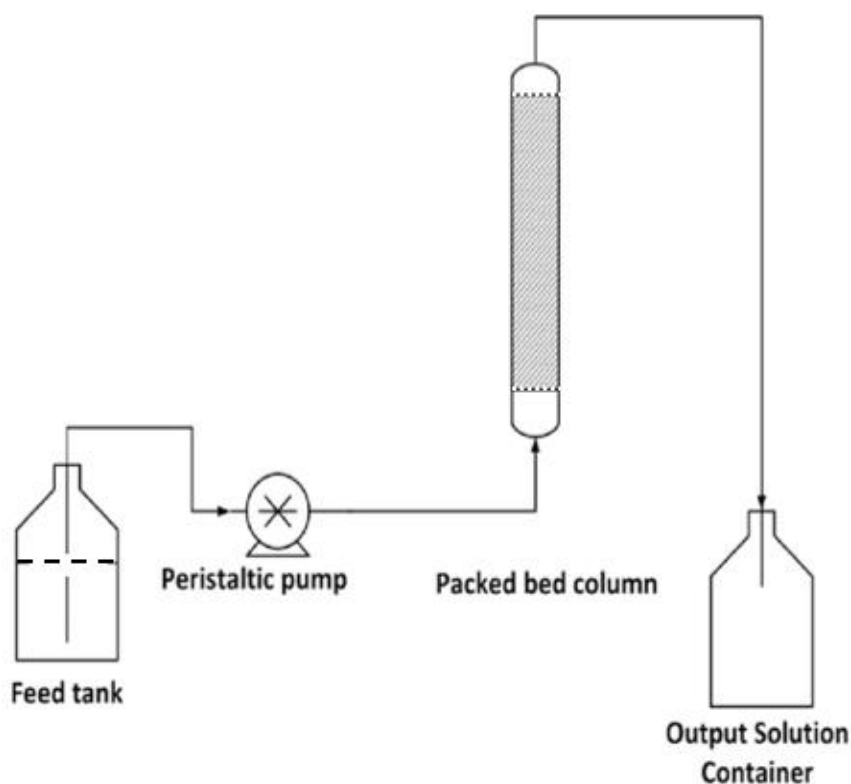


Figure 3.3 Schematic view of fixed bed adsorption column

3.5 Analysis of prepared synthetic and ERCO brine solution

3.5.1 DPD colorimetric method

The initial and residual concentrations of FC, MC, DC and TC were analyzed using DPD colorimetric method using UV spectrophotometer at 515 nm. The amount of absorbance was adjusted by calibration curve (Appendix). The amount of combined chlorine was determined by taking sum of MC, DC and TC concentrations. Removal (%) of free chlorine and combined chlorine was determined using the following equations (3.3-3.5):

$$\text{Chloramine removal (\%)} = \frac{MC_{\text{Highest}} - MC_{\text{Final}}}{FC_{\text{Initial}}} \times 100 \quad (3.3)$$

$$\text{Combined chlorine} = FC + MC + DC + TC \quad (3.4)$$

$$\text{Combined chlorine removal (\%)} = \frac{\text{Combined Chlorine}_{\text{Initial}} - \text{Combined Chlorine}_{\text{Final}}}{\text{Combined Chlorine}_{\text{Initial}}} \times 100 \quad (3.5)$$

3.5.2 Determination of Ammonia in brine by Spectrophotometry

The initial and residual concentrations ammonia in brine was determined by method PE-04-03 using UV spectrophotometer at 655 nm.

3.5.3 Effects of humic acid on chloramine removal

To study the effects of organic content on chloramine removal, humic acid was added into the reaction mixture as a source of organic carbon. The method developed by Li, et al (2009) was used for the preparation of samples.

3.5.4 Characterization of activated carbon samples

The activated carbon samples (fresh and exhausted) were characterized using BET, FTIR, XRD and XPS in Catalyst Characterization laboratory at Department of Chemical and Biological Engineering, University of Saskatchewan. The exhausted activated carbon samples were collected via filtration after the completion of batch adsorption experiments.

The surface area of the activated carbon degassed at 300°C for 3 h was computed using the Brunauer-Emmett-Teller (BET) method, whereas the pore –size distribution was determined using Barret –Joyner-Halenda (BJH) model.

Small angle X-ray diffraction (SXRD) patterns were determined on a D8 Advance Powder Diffractometer equipped with GE monochromator. The samples were scanned from 2° to 90° with a step size of 0.01.

The FT-IR spectra of the composites were recorded on Fourier transform spectrometer (Vertex 60 Bruker, Germany).

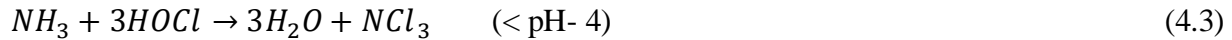
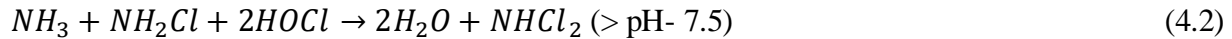
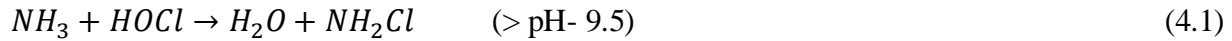
X-ray photoelectron spectroscopy (XPS) measurements were collected using a Kratos (Manchester, UK) AXIS supra system at Saskatchewan Sciences Structural Centre (SSSC). All survey scan spectra were collected in the 5- 1200 binding energy range in 1 eV steps with a pass energy of 160 eV.

4. RESULTS AND DISCUSSION

4.1 Removal of chloramines from synthetic solution using UV technology

4.1.1 Optimization of reaction parameters in UV-system

A total of 20 experiments were designed for the optimization of reaction conditions by varying solution pH, reaction time and ammonia to chlorine ratio according to Table 3.3. All of experiments were performed in duplicates, and some of them in triplicates. The results were analyzed in terms of combined chlorine removal (%). Fig. 4.1 shows the correlation between ammonia to chlorine ratio to solution pH. It was observed that the combined chlorine removal increased with increase in ammonia to chlorine ratio. However, combined chlorine removal (%) found to decrease with an increase in solution pH. This can be explained based on Equations 4.1-4.3.



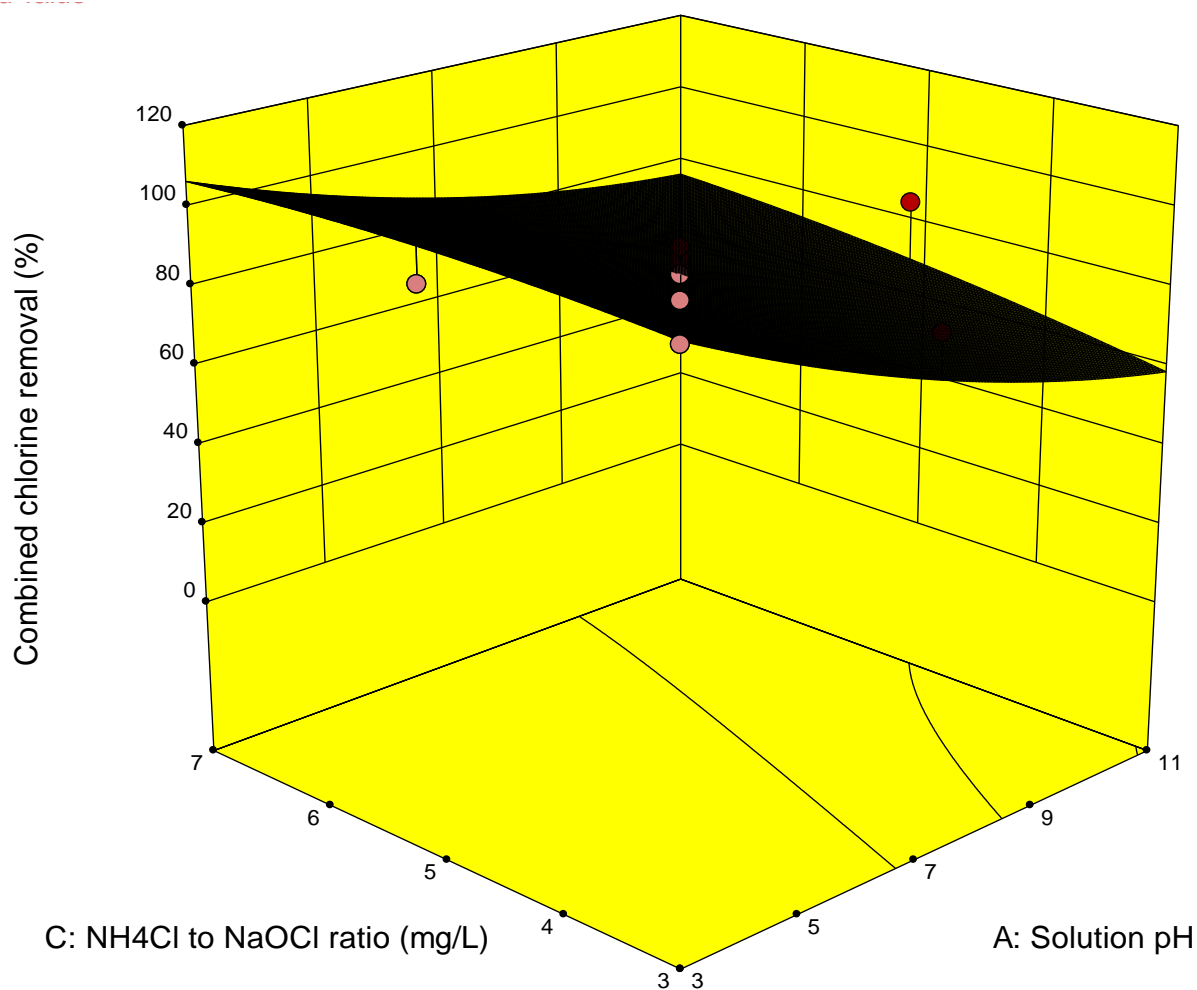


Figure 4.1 Effects of ammonia to chlorine ratio and solution pH on combined chlorine removal

It can be seen from Equation 4.3 that acidic pH favors the formation of TC. Since, TC is more volatile than DC and MC, it can easily evaporate from the reaction mixture. This might be the reason for more combined chlorine removal at acidic pH.

Also, it was observed that reaction time depended on solution pH. It was found that the combined chlorine removal increased with increase in reaction time from 15 to 30 min. Further increase in reaction time up to 45 min leads to a slight decrease in combined chlorine removal.

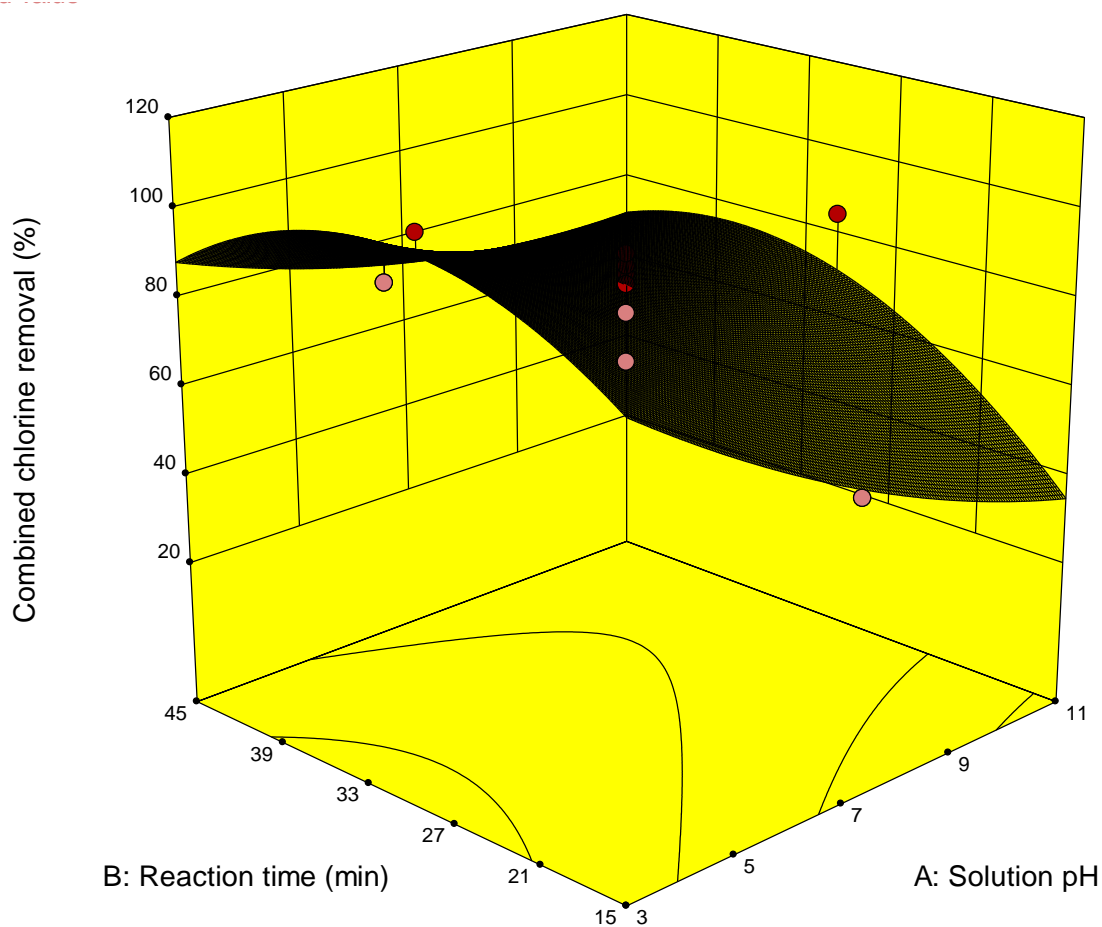


Figure 4.2 Effects of reaction time and solution pH on combined chlorine removal

Fig 4.2 shows the correlation between reaction time and solution pH. It was observed that the combined chlorine removal increased with increase in reaction time from 15 to 30 min. Further increase in reaction time up to 45 min lead to a slight decrease in combined chlorine removal (%).

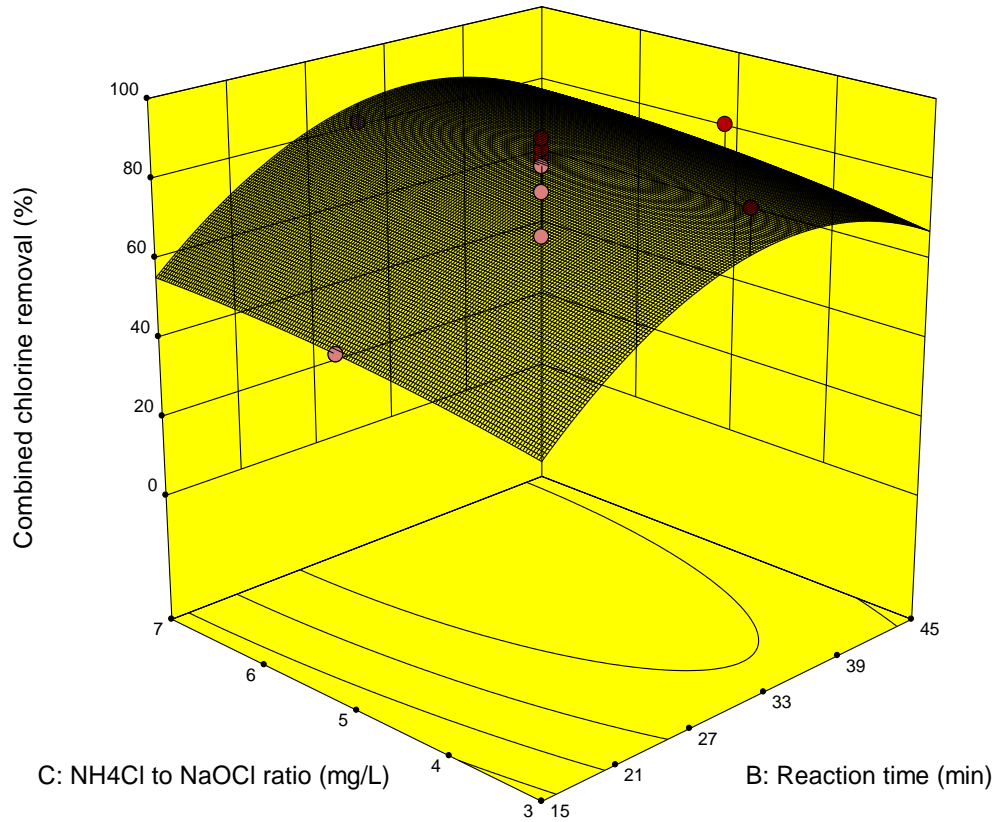


Figure 4.3 Effect of ammonia to chlorine ratio and reaction time on combined chlorine removal

4.1.2 Statistical analysis

The results of analysis of variance (ANOVA) for statistical analysis of combined chlorine removal (%) in UV-system has been presented in Table 4.1. Model adequacy was tested through p-values, F-values and lack-of-fit. The lack-of-fit terms were non-significant (more than 0.05), indicating that the models were valid in the present study. The R-squared-values of 0.88 indicate that there is good correlation between different reaction parameters. The standard deviation is 8.77. The model was explained by quadratic equation, where A, B and represents solution pH, reaction time and ammonia to chlorine ratio, respectively.

$$\begin{aligned} \text{Combined chlorine removal (\%)} = & + 82.69 - 17.43 *A + 9.33*B + 4.41*C + 9.04*AB + 0.94*AC \\ & + 3.04 *BC + 7.92 *A^2 - 16.93 *B^2 - 3.9 *C^2 \end{aligned} \quad (4.4)$$

Based on this Equation 4.4, reaction time and ammonia to chlorine ratio are positively correlated with combined chlorine removal, whereas solution pH is negatively correlated with combined chlorine removal.

Table 4.1 Analysis of variance for UV-system

Source	Sum of Squares	df	Mean Square	F Value	p-value (Prob > F)	Result
Model	6067.3	9	674.9	8.7	0.001	significant
A-Solution pH	3038.9	1	3038.9	39.5	< 0.0001	
B-Reaction time	869.9	1	869.9	11.3	0.007	
C-NH ₄ Cl to NaOCl ratio	194.4	1	194.4	2.5	0.14	
AB	653.8	1	653.8	8.5	0.02	
AC	7.01	1	7.0	0.09	0.77	
BC	74.1	1	74.1	0.9	0.3	
A ²	172.4	1	172.4	2.2	0.16	
B ²	787.8	1	787.8	10.2	0.009	
C ²	41.9	1	41.8	0.5	0.48	
Residual	769.2	10	76.9			
Lack of Fit	377.1	5	75.4	0.96	0.52	not significant
Pure Error	392.1	5	78.4			
Cor Total	6936.9	19				
R-Squared	0.88					
Adeq Precision	12.3					
Std. Dev.	8.77					

4.1.3 Effects of operational conditions on FC, MC, DC and TC concentrations

Figures 4.4 - 4.7 shows the effects of reaction parameters on FC, MC, DC and TC concentrations in the reaction mixture. It can be seen from Fig. 8 that more than 90 % FC removal is obtained under all reaction conditions, except in 4 points at 1:7 ammonia to chlorine ratios. The lower FC removal in these samples might be due to presence of higher initial concentrations of FC in the reaction mixture at 1:7 ammonia to chlorine ratio compared to 1:3 and 1:5.

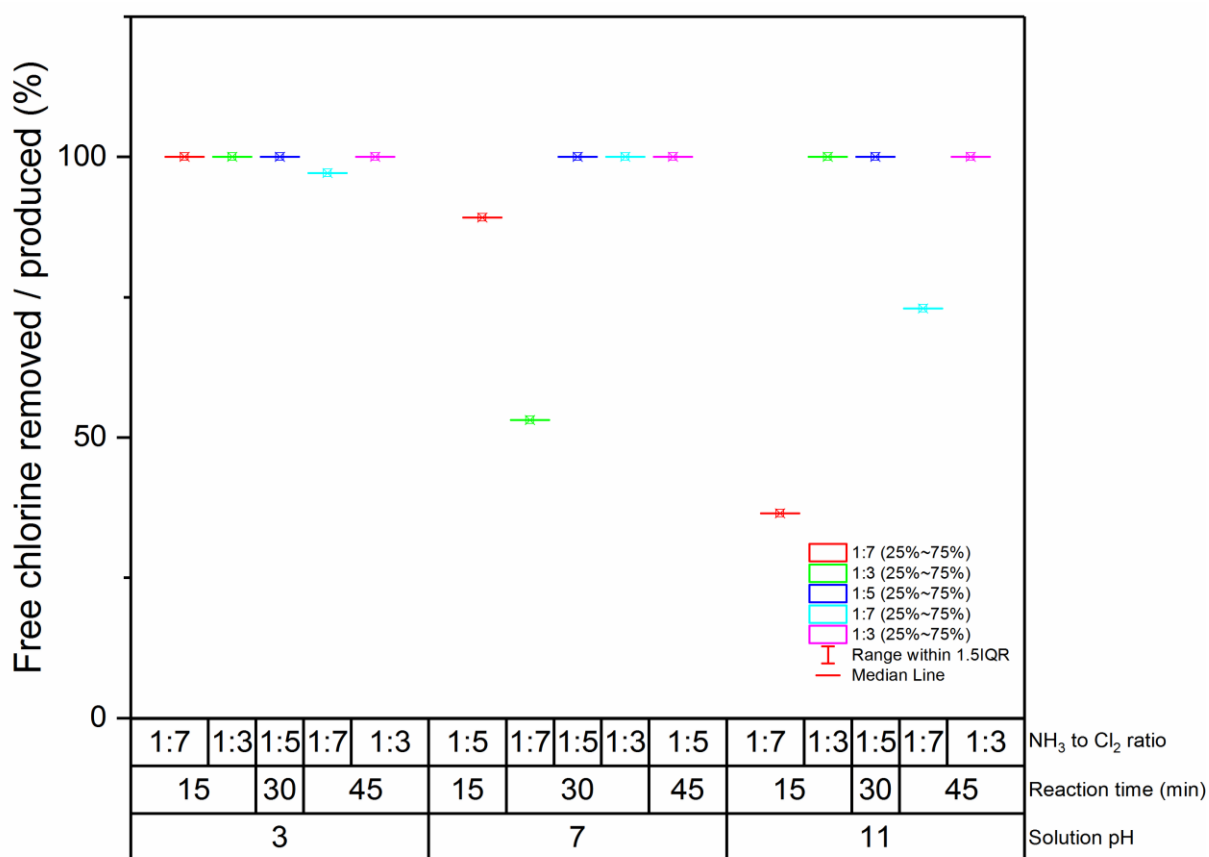


Figure 4.4 Effects of reaction parameters on free chlorine concentrations

Figure 4.4 shows the effect of reaction conditions on MC concentrations. It was found that MC removal (%) is positively correlated with reaction time and ammonia to chlorine ratio, whereas

it is negatively correlated with solution pH. The negative values at pH 11 indicate that the amount of MC produced in the reaction mixture is more than amount of MC removed. This is in-agreement with the literature reports that the alkaline pH favors the formation of MC in the reaction mixture (Zhang et al., 2015; Xue et al., 2017).

Figure 4.5 shows the effect of UV treatment on DC concentrations in the reaction mixture. It was observed that alkaline pH favors the removal of DC from reaction mixture. It can be seen from Fig. 6 that complete removal of DC was observed at pH 11, irrespective of UV reaction time.

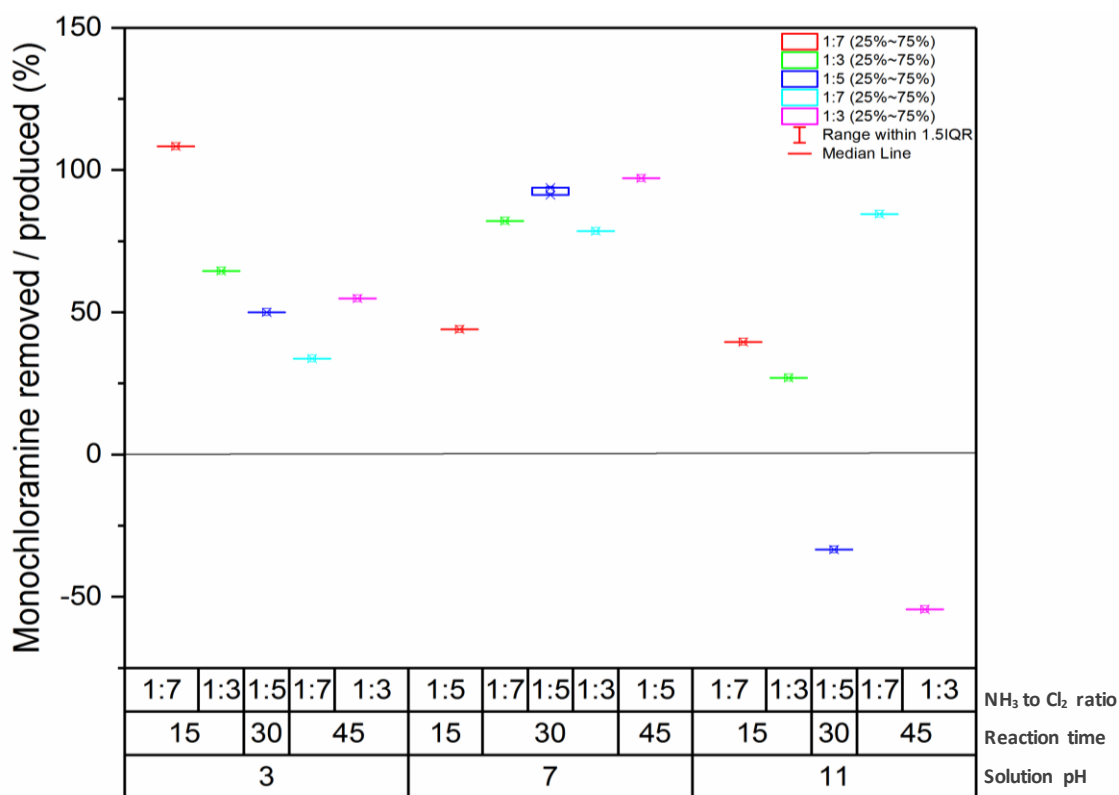


Figure 4.5 Effects of reaction parameters on monochloramine concentrations

Further, DC removal (%) found to increase with increase in ammonia to chlorine ratio from 1:3 to 1:7 at both pH 3 and pH 7. This might be due to the conversion of DC into TC in presence of high concentrations of Cl₂ in reaction mixture.

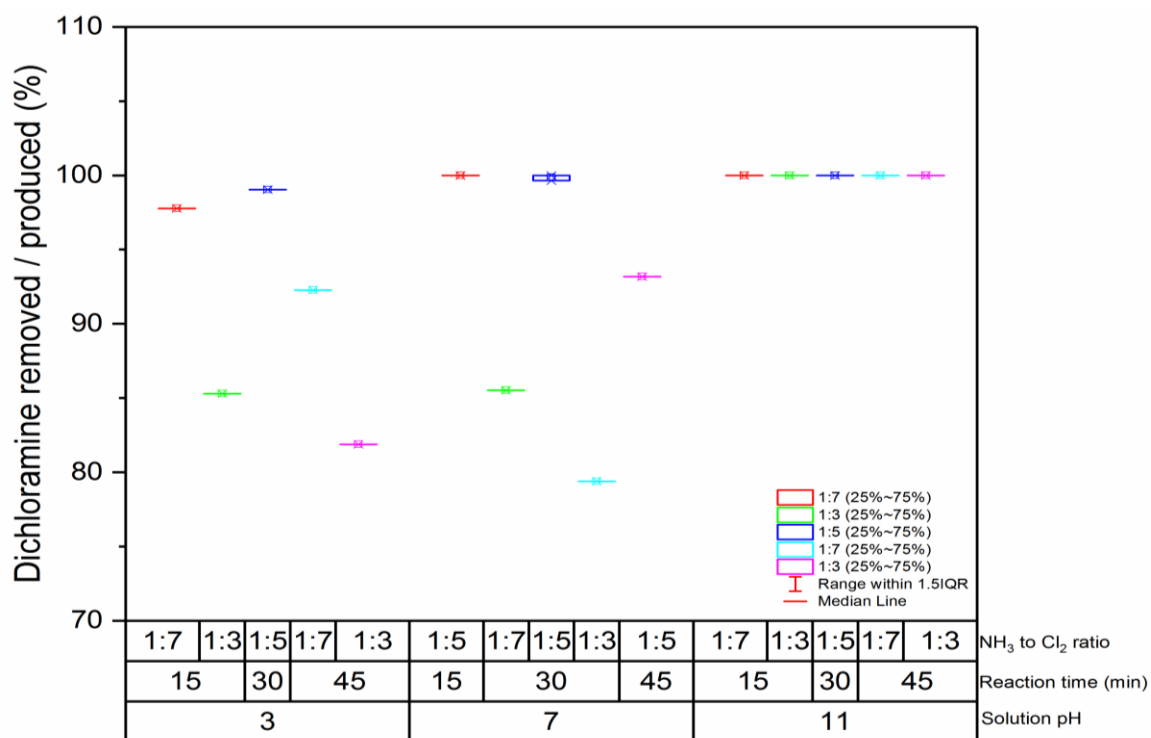


Figure 4.6 Effects of reaction parameters on dichloramine concentrations

Figure 4.7 shows the effects of UV treatment on TC concentrations in the reaction mixture. Maximum removal of TC was obtained at acidic pH. The removal of TC found to increase with increase in reaction time from 0 to 30 min, further increase in reaction time doesn't have much impact of TC removal.

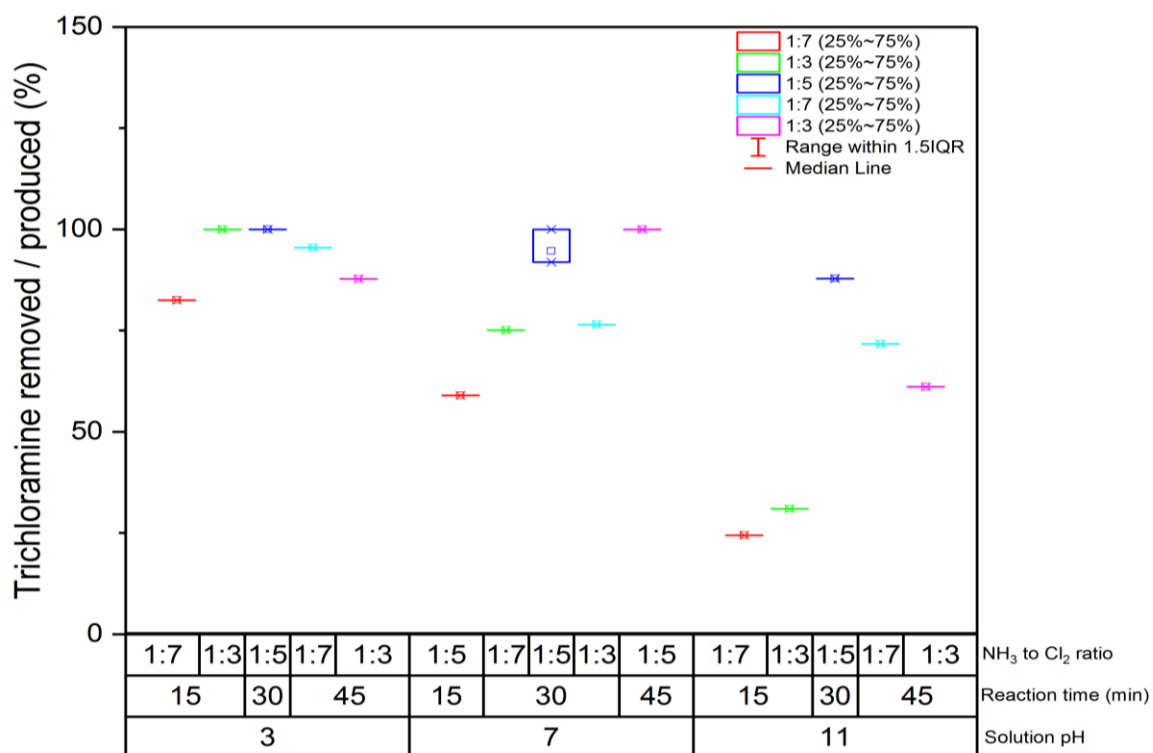


Figure 4.7 Effects of reaction parameters on trichloramine concentrations

4.1.4 Kinetics study

Kinetics study was performed to study the effect of UV treatment time (0 min to 30 min) on FC, MC, DC and TC removal at different ammonia to chlorine ratios (1:3 to 1:7). It was found that concentration of all four compounds decreased with an increase in reaction time from 0 to 30 min, irrespective of ammonia to chlorine ratios. Irrespective of ammonia to chlorine ratio, 100 % removal of FC, MC and DC was observed in all the samples. Complete removal of TC was only observed at 1:7 ammonia to chlorine ratio. As, it can be seen from Fig. 4.8 that some residual concentrations of TC was still remaining in the reaction mixture at 1:3 and 1:5 ammonia to chlorine ratio.

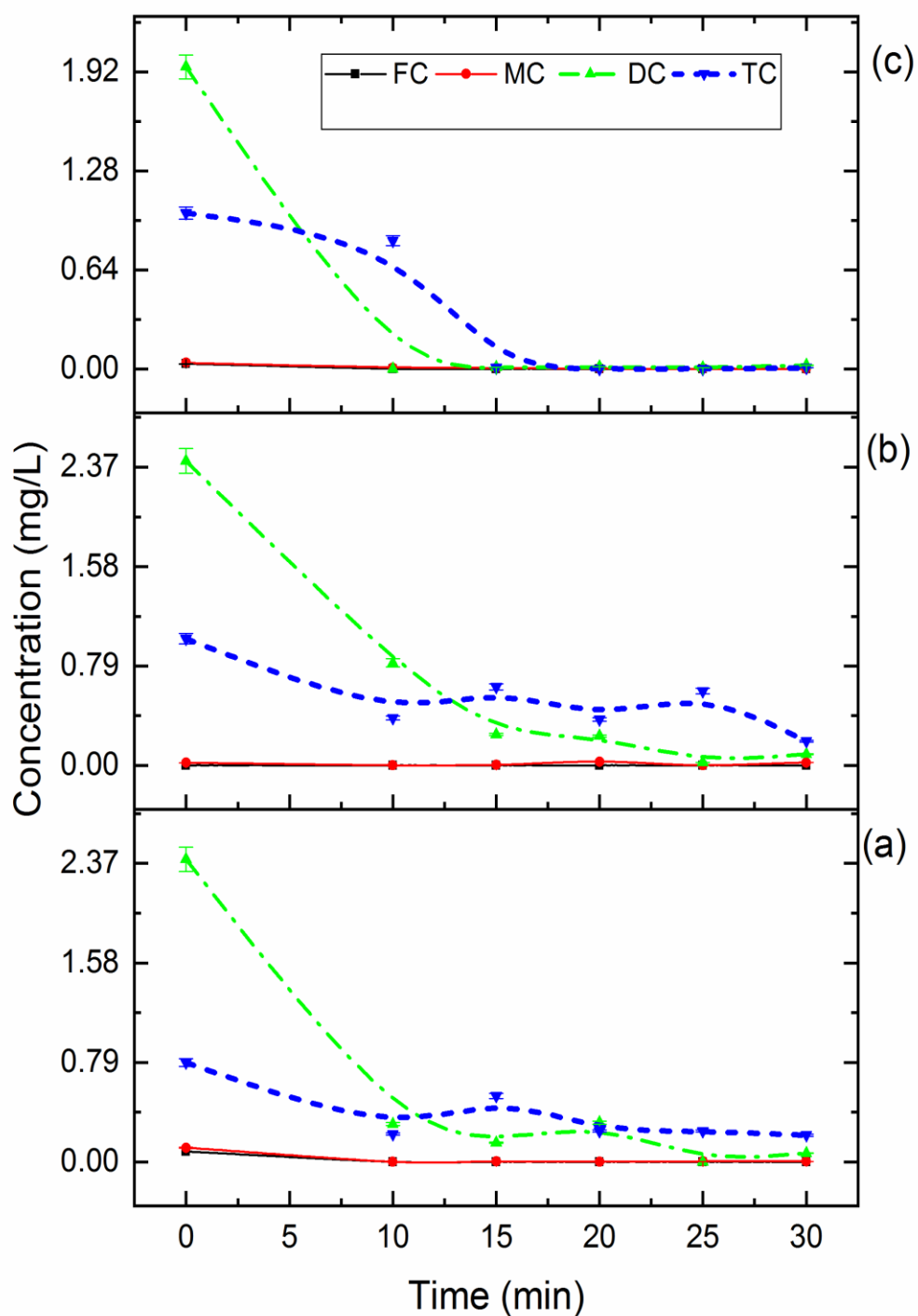


Figure 4.8 Kinetics study for the removal of free chlorine and chloramines at different ammonia to chlorine ratios in synthetic solution: (a) 1:3; (b) 1:5 and (c) 1:7. (Reaction conditions: pH 6; reaction time 0 to 30 min; ammonia to chlorine ratio 1:3 to 1:7, reaction temperature 25 °C)

4.1.5 Effects of temperature on FC, MC, DC and TC concentrations

Effect of reaction temperature on free chlorine, MC, DC and TC concentrations during UV adsorption was studied by varying the reaction temperature from 5.4°C to 45.4°C. It was observed from the previous experiments that maximum TC adsorption occurs at pH 3, thus all of experiments were performed at pH 3.

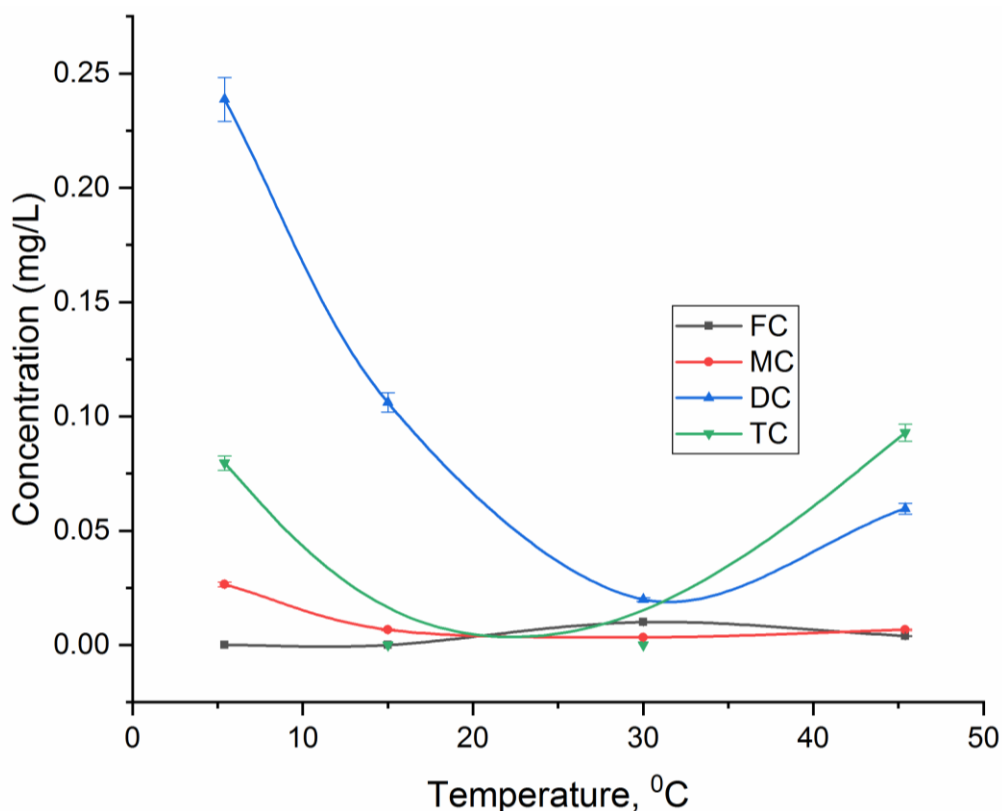


Figure 4.9 Effects of temperature on FC, MC, DC and TC concentrations (Reaction conditions: Solution pH – 3; reaction time- 30 min; ammonia to chlorine ratio – 1:5, reaction temperature – 5.4 °C, 15 °C, 30 °C, 45.4 °C).

Figure 4.9 illustrates the concentrations of FC, MC, DC and TC at different temperature (5.4 °C, 15 °C, 30 °C, 45.4 °C). FC concentrations found not affected by temperature. Meanwhile, MC, DC and TC concentrations starts decreasing with rising temperature and reached maximum of adsorption at 30 °C. With increasing temperature, the removal of DC and TC decreased (Chen

et al, 2011). At temperature ≤ 30 , UV irradiation of TC cleaves the N-Cl bond in a first step, leading to a Cl^\bullet and NCl_2^\bullet radical. In aqueous solution, Cl^\bullet can react with H_2O to form $^\bullet\text{OH}$ or react as an oxidant with other species. It is reported that the increase in temperature increases the collision frequency between the chloramine and free radicals, which results in increase in the removal of chloramine from solution (Li et al., 2010). However, at higher temperature ($> 30^\circ\text{C}$), the reason of increasing of DC and TC concentrations is not clear.

4.1.6 Effects of presence of organic contaminant on chloramine removal from brine by UV adsorption

Humic acid was used as a source of organic matter. 5 samples of brine were prepared with 1, 2.5, 5, 7.5 and 10 mg of humic acid and pH was set at 3 as a best condition for UV treatment. Each of sample was consistently exposed to UV radiation for 30 minutes.

It was found that after UV treatment, the chloramines were completely removed from brine with presence of humic acid irrespectively of its concentration in reaction mixture. This indicates that the presence of organic matter does not influence the efficiency of chloramine removal using UV-treatment.

The initial and residual concentrations ammonia group NH_4 in brine were determined by method PE-04-03 using UV spectrophotometer at 655 nm.

4.2 Adsorption of chloramines on activated carbons

4.2.1 Batch study. Effects of pH at different ammonia to chlorine ratios

The batch experiments were performed on an incubator shaker maintained at 25°C and agitation speed of 120 rpm. To perform the experiments, 50 mg of granular activated carbon

(GAC) was added to 250 mL conical flasks containing 50 mL of chloramine solution maintained at pH 2.4, 3, 5, 6, 7, 9 and 11 for 24 h.

The experimental results showed efficient removal of chloramine by GAC at pH 6 and pH 9. 100 % chloramine removed at pH 6. It was found that pH range did not effect on the adsorption capacity of activated carbon, however, the pH level affected the chloramine removal. This study agreed with Kusmierc and Swiatkowski (2015) that pH does not drastically influence on the adsorption process.

Table 4.2 Results of pH experiments

pH	Conc.TC, (mg/L)	Conc.Total, (mg/L)	%Removal		Adsorbed amount (mg/mg)	
			TC	Total	TC	Total
2.4	0.13	0.14	90	92	1.12	1.66
3	0.06	0.51	97	77	1.96	1.74
5	0.05	0.05	93	93	0.71	0.73
6	0	0.03	100	98	1.17	1.77
7	0.08	0.10	95	95	1.42	1.76
9	0	0.01	100	99	0.45	0.57
11	0	0.27	83	86	1.50	1.62

4.2.2 Effects of adsorbent dosage

To perform the experiments, a predetermined amount of granular activated carbon (0.5 g - 1.5 g) was added in 250 mL conical flask containing 50 mL of chloramine solution at ammonia to chlorine ratio of 1:5 and optimum pH 6 and agitation speed of 120 rpm for 24 h.

The study of effect of dosage of GAC on chloramine removal found that higher mass of GAC favored higher extent of chloramine removal. It may be observed from Figures 4.10 and 4.11. At higher adsorbent dosage, more active sites are available for removal of chloramines that results in an increase in removal of chloramines from reaction mixture.

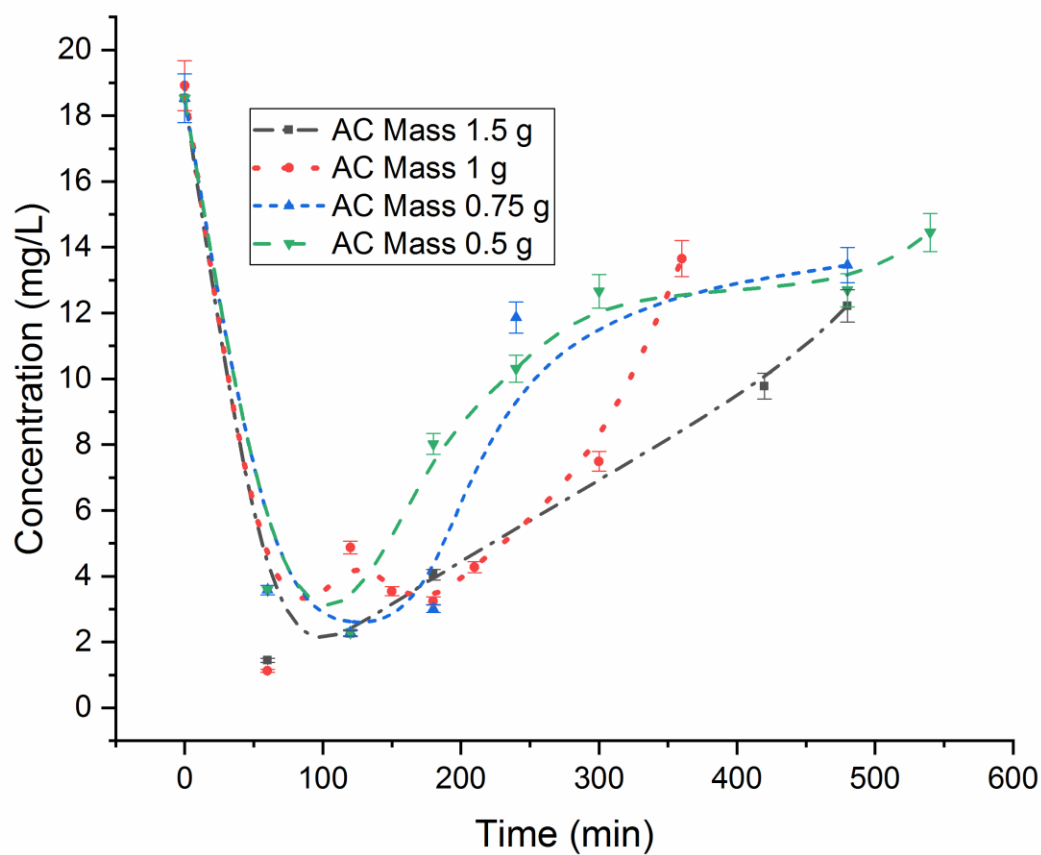


Figure 4.10 Effect of dosage of AC on total chloramine adsorption (Reaction conditions: solution pH – 6; ammonia to chlorine ratio 6:30; AC dosage – 0.5-1.5 g)

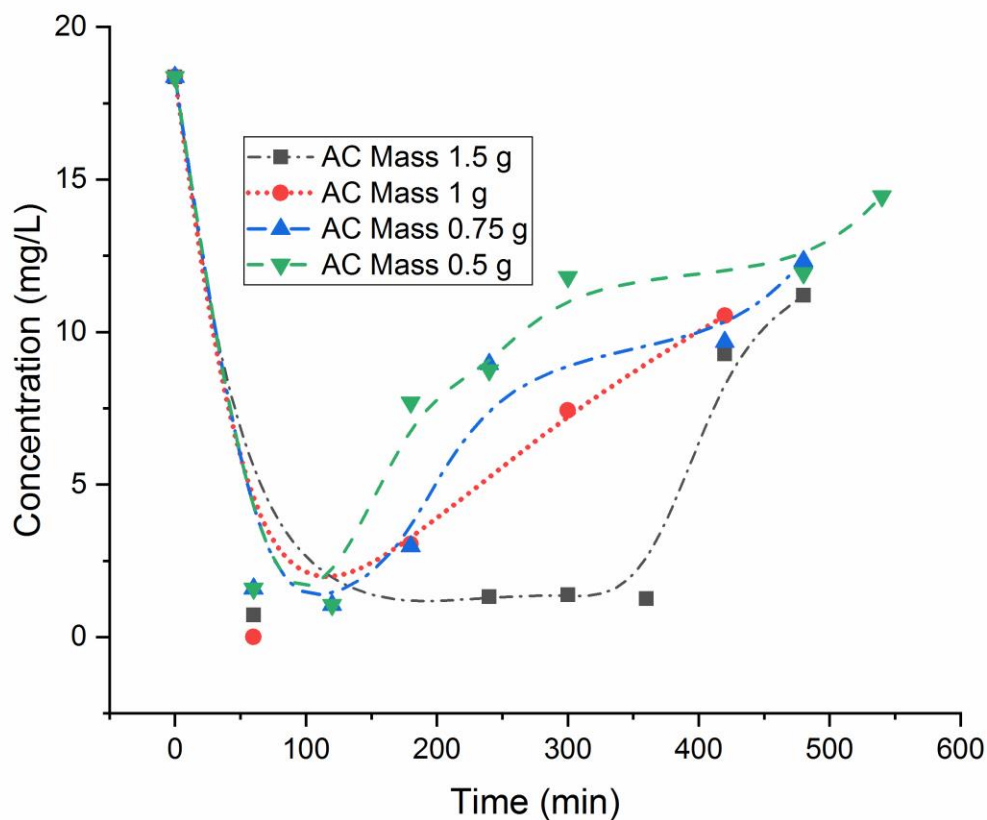


Figure 4.11 Effects of dosage of AC on trichloramine (TC) adsorption (Reaction conditions: solution pH – 6; ammonia to chlorine ratio 6:30; AC dosage – 0.5-1.5 g)

4.2.3 Effects of ammonia to chlorine ratio on chloramine removal

For the isotherm study, the batch equilibrium experiments were performed in an incubator shaker using 250 ml conical flasks, at optimum chloramine concentration of 2 g/L with ammonia to chlorine ratio of 1:5, 2:10, 3:15, 4:20, 5:25 and 6:30.

With increasing ratio of ammonia to chlorine, amount of FC after treatment was increased, amount of MC after treatment decreased, DC formation did not change. Increasing ratio of ammonia to chlorine did not influence on DC formation. With increasing ratio of ammonia to

chlorine, amount of TC after treatment decreased, Fig.4.12. Wu et al. (2018) in their studies of adsorption on activated carbons found that ratio affected the adsorption. With increasing ratio of ammonia to chlorine, % removal decreased.

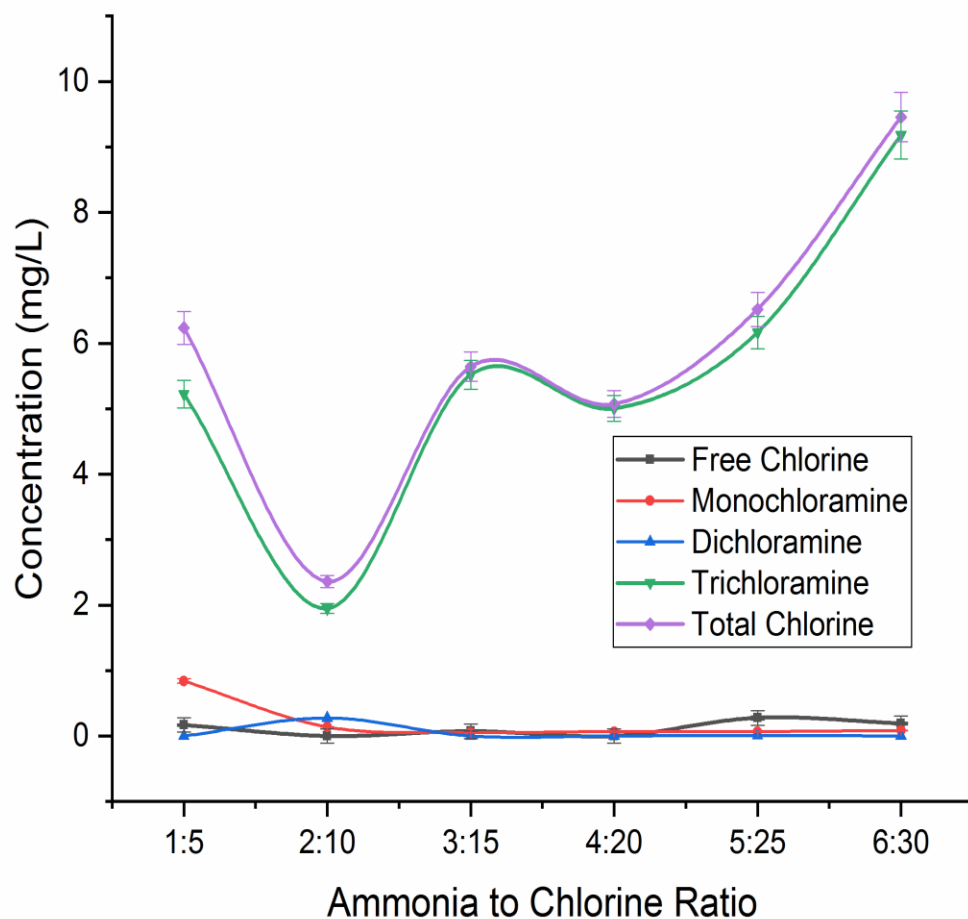


Figure 4.12 Effects of ammonia to chlorine ratio on chloramine removal (Reaction conditions: solution pH – 6; time – 24 h; AC dosage – 2 g/L; Temperature - 25°C)

At lower pollutant concentrations, high energy adsorption sites are available for chloramine removal resulting in high energy adsorption capacity, while with increasing initial concentration the high energy adsorption sites became saturated and more pollutant left unadsorbed in solution.

Overall, with increasing of ammonia to chlorine ration, the total concentration of chloramine increased.

4.2.4 Process optimization study

The concentration 2 g/L, pH 6, ammonia to chlorine ratio 1:5 and agitation speed of 120 rpm were found as optimum conditions of reaction for trichloramine removal. The results of experiments showed that the breakthrough point was reached at 15 minutes with 93 % of chloramine removal

4.2.5 Batch experiments with brine

For all of experiments with brine, the solution was taken from the sampling point and was used for 14 days. The collected brine was stored at 4°C in dark.

The initial pH of brine solution was 11.4. The brine solution was spiked with different concentrations of ammonia (0 to 0.2 mg/L). It was found that the concentration of ammonia in brine was 0.43 mg/L after two hours of sampling, and it was slightly decreased to 0.3 mg/L after 120 hours. The trichloramine concentrations in brine was found to be 0.8 mg/L and total chloramine concentration was 1.09 mg/L.

For batch experiment were used optimum parameters which were found during investigations of synthetic solution. The optimum conditions are: pH 6, temperature of 25 °C, mass of GAC - 50 mg on 50 mL of solution, agitation speed - 120 rpm (incubator shaker), Table 4.3. The % removal of chloramines was found to decrease from 93% (synthetic solution) to 88% (brine).

Table 4.3 Batch experiments with brine

Parameter	Chloramine concentration, mg/L	Chloramine (Total) % Removal
initial	1.09	88 %
final	0.12	

This might be due to the presence of large amount of salt content in brine solution. The highest salt content might have clogged the pores of activated carbon resulting to decreasing its adsorption capacity (see Fig. 4.13)



Figure 4.13 –Solid salt precipitation in batch experiments of brine with GAC

4.1.6 Effects of temperature

The results of experiments showed that percent removal of chloramine is drastically increasing with increasing temperature (Figures 4.14 and 4.15). The chloramine removal increases with an increase in temperature is due to following reasons: increased temperature causes increase in the rate of diffusion of adsorbate molecules across boundary layers to internal pores of the adsorbent due to decrease in viscosity of the solution (Table 4.4).

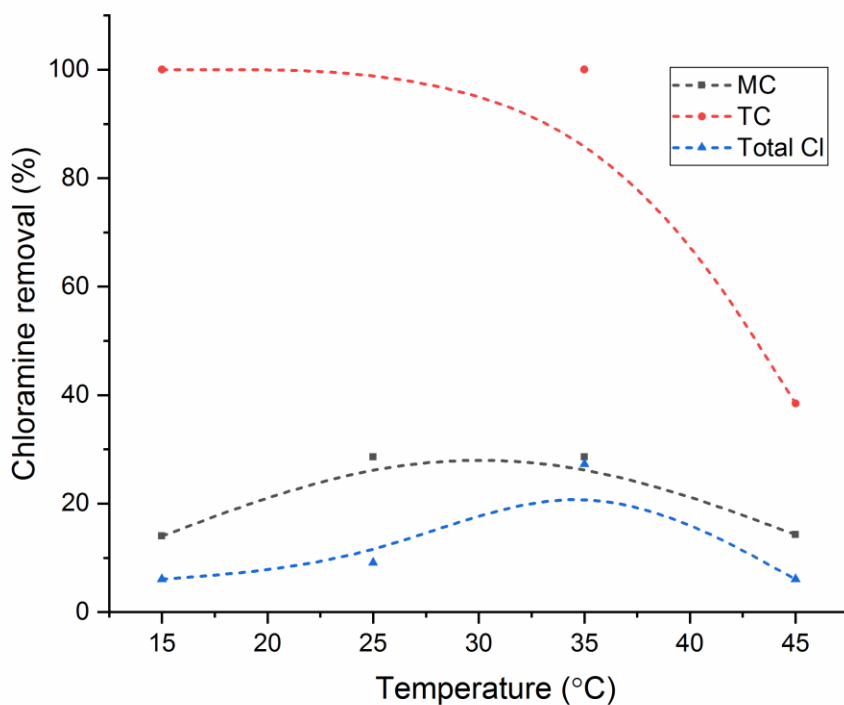


Figure 4.14 Temperature effect on chloramine removal from brine
(Reaction conditions: solution pH – 6; Brine; AC dosage – 50 mg of AC /50 mL of brine;
Temperature – 15 – 60 °C)

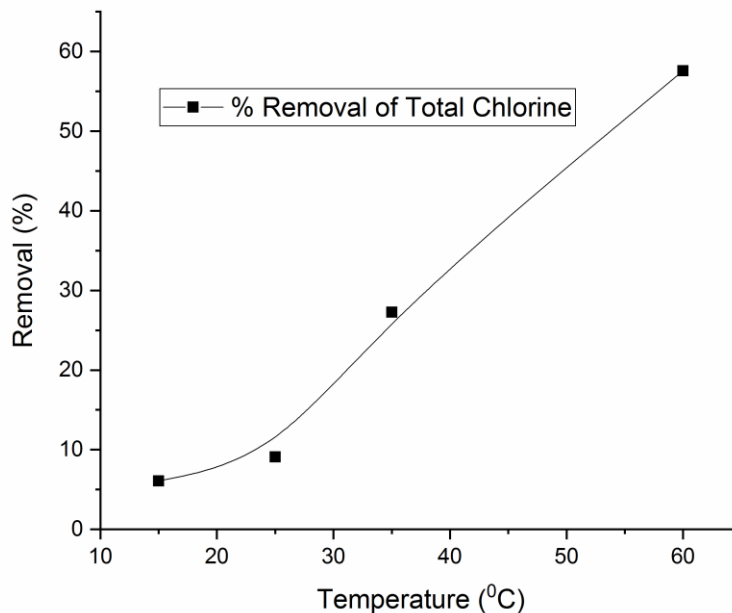


Figure 4.15 Effects of temperature on % removal of chloramines by activated carbon (Reaction conditions: solution pH – 6; Brine; AC dosage – 50 mg of AC /50 mL of brine; Temperature – 15 – 60 °C)

Table 4.4 Density and viscosity of freshwater and brine solutions at different temperatures (26th ITTC Specialist Committee on Uncertainty Analysis)

Temperature (°C)	Freshwater		Sea water (Concentrated brine)	
	Density (kg/m ³)	Viscosity (Pa.s)	Density (kg/m ³)	Viscosity (Pa.s)
15	999.10	0.0011	1026.1	0.001
25	997.05	0.0008	1023.3	0.0009
35	994.03	0.0007	1019.1	0.0008
40	992.21	0.0006	1018.0	0.0007

Further, the effects of temperature on brine chemistry was not studied. However, it is speculated that changes in temperature might not have any effect on overall brine chemistry except changing its physical properties like density and viscosity.

4.3 Adsorption on activated carbons in a column study

4.3.1 Effects of flow rate

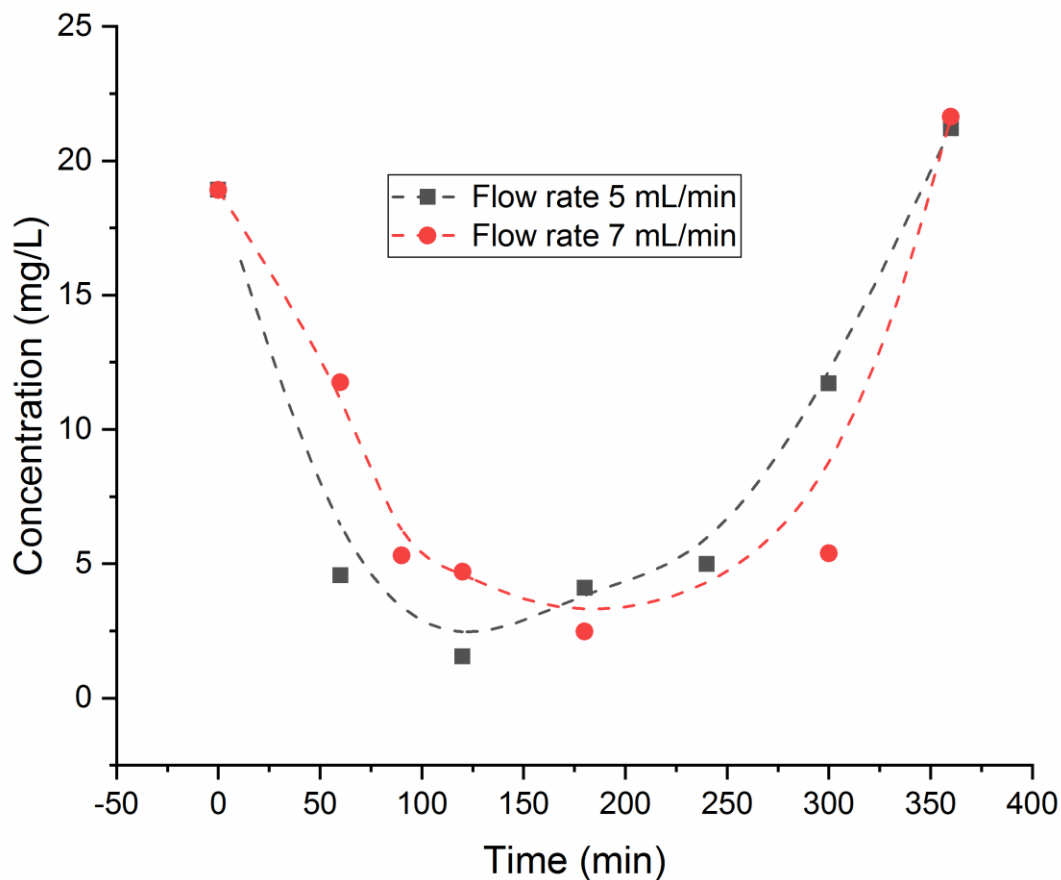


Figure 4.16 Effect of flow rate on total chloramine adsorption
(Reaction conditions: solution pH – 6; ammonia to chlorine ratio 6:30; AC dosage – 1 g)

Synthetic solution

The effect of flow rate on chloramine removal by GAC was studied at flow rate of 5 and 7 mL/min, while the pH level of solution and dosage of activated carbon were held constant at 6 and 1 g respectively. The breakthrough curves obtained by plotting effluent chloramine concentration

versus time at different flow rates and its effect on total chlorine and trichloramines uptake are shown in Figure 4.16 and 4.17.

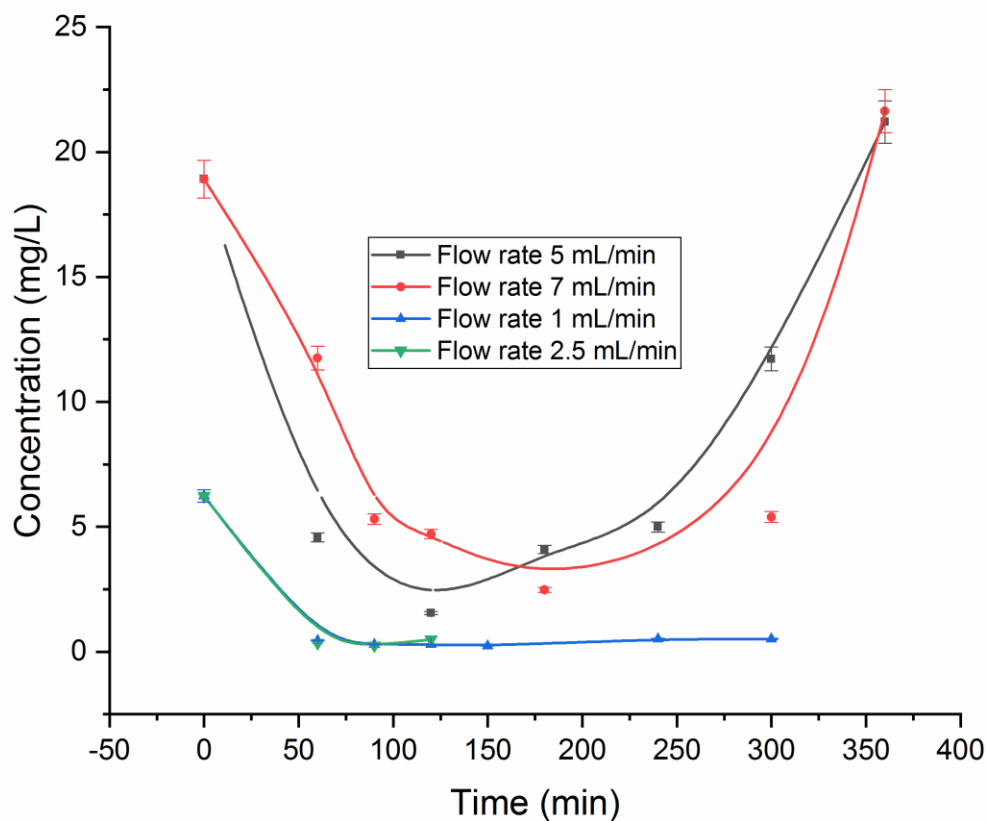


Figure 4.17 Effect of flow rate on trichloramine adsorption (Reaction conditions: synthetic solution pH – 6; ammonia to chlorine ratio 6:30 and 1:5; AC dosage – 1 g)

It was found that adsorption efficiency was higher at lower flow rate and time to achieve the breakthrough point decreases, which is indicated on Figure 4.17. The possible reason of this behavior is that at lower flow rate the contact time of the contaminants in the column is increased leads to increasing efficiency for an adsorption (see Figure 4.18).

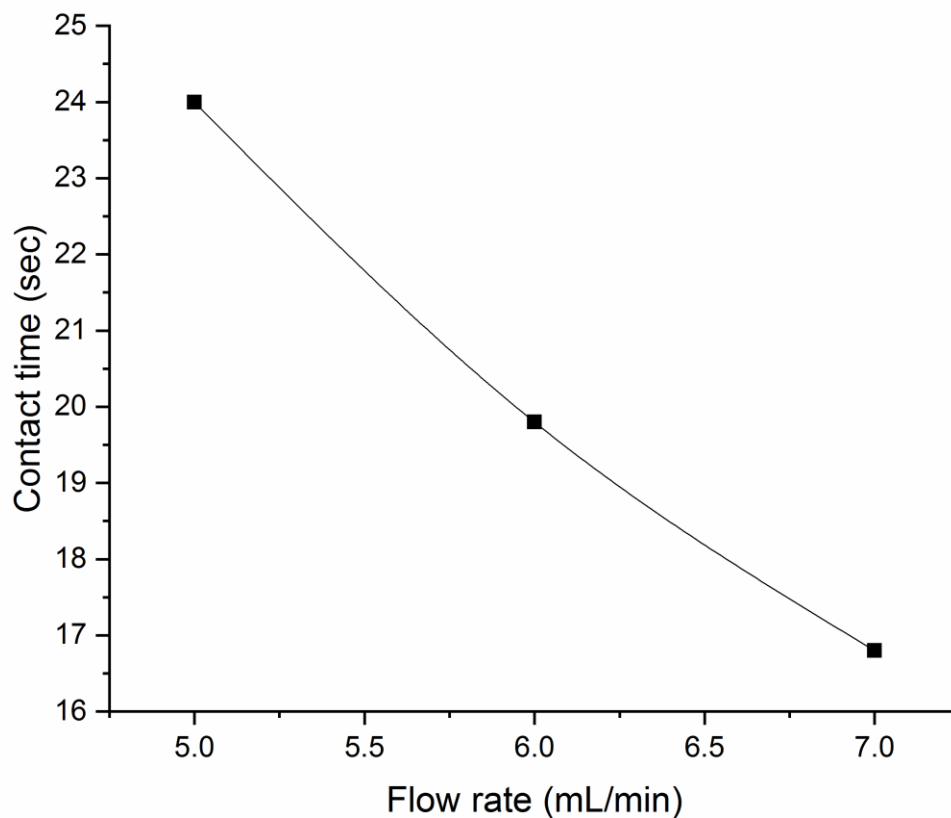


Figure 4.18 Dependence contact time from flow rate. (Reaction conditions: synthetic solution pH – 6; ammonia to chlorine ratio 6:30; AC dosage – 1 g)

Brine solution

The adsorption experiments using brine solution were performed at optimum conditions obtained from batch experiments using synthetic solution. As mentioned in section 4.2.1, the pH only influence the chloramine formation and not the process of adsorption, thus, the pH level of real brine was not adjusted. For the column experiments, 1 g of GAC was used and experiments were conducted at room temperature 25 °C, pH 11 and flow rate 6 mL/min.

Experiments with flow rate showed up good results, the % removal of 89% of total chloramines (after 24 h treatment with flow rate of 6 mL/min) was obtained as shown on Figure 4.19.

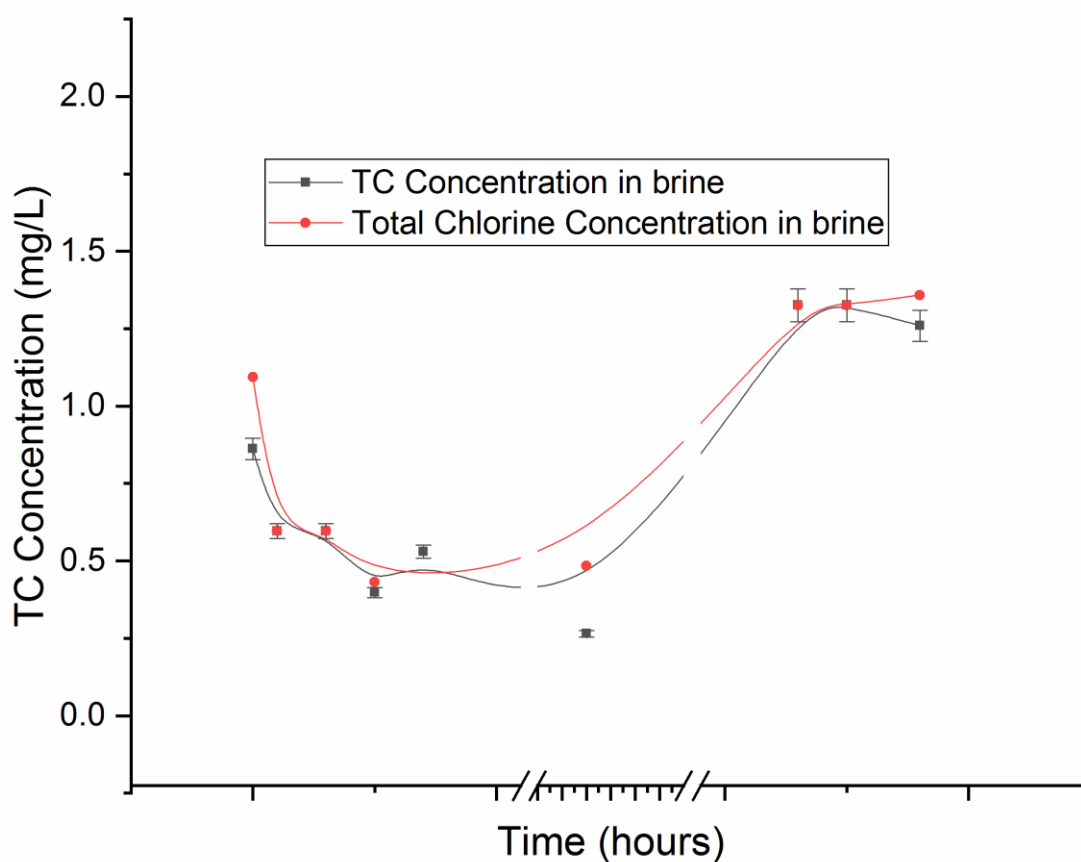


Figure 4.19 Column study on brine. (Reaction conditions: solution pH – 11; Brine; AC dosage – 1 g, temperature - 25°C, flow rate - 6 mL/min)

For the efficient chloramine removal from saturated sodium chloride brine needs continuous fed to prevent insoluble precipitations to occupy and clog the pores of activated carbon.

4.3.2 Effects of reaction time

The effects of reaction time at different ammonia to chlorine ratio on the chloramine removal were studied at optimum reaction conditions such as pH 6, temperature 25°C, flow rate 6 mL/min.

It was found that at lower ammonia to chlorine ratio than less time needed to achieve breakthrough point. The optimum ratio ammonia to chlorine was found 6:30. Fig. 4.20 illustrates ammonia to chlorine ratios investigations.

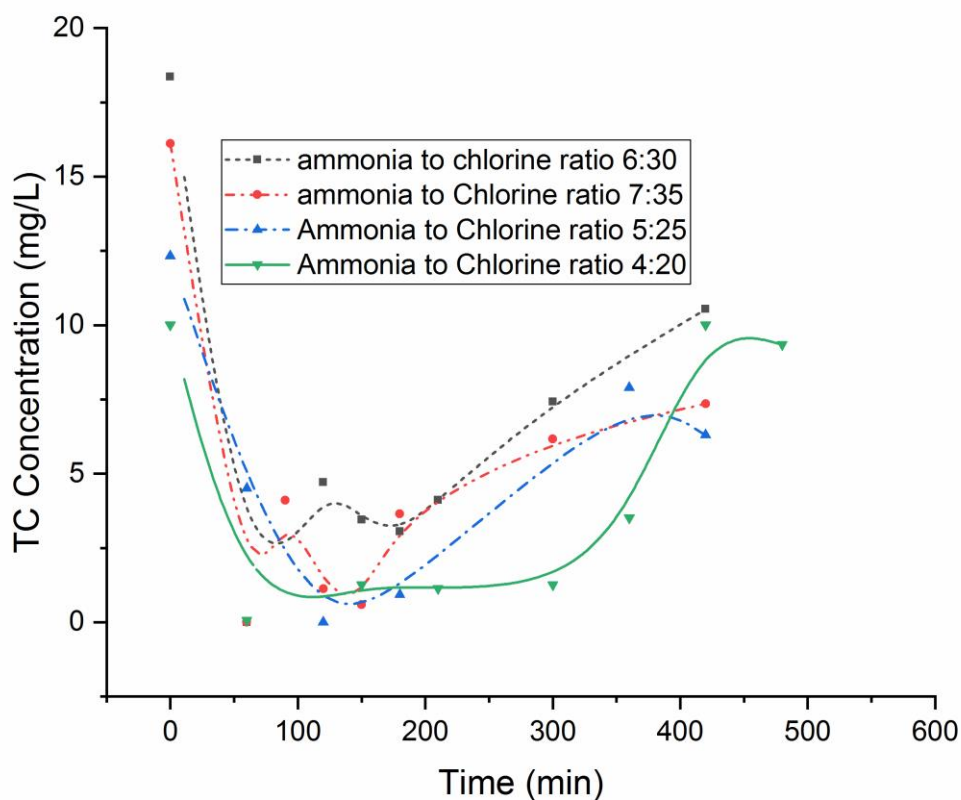


Figure 4.20 Effects of ammonia to chlorine concentrations at ratio of 1:5 on trichloramine (TC) adsorption (Reaction conditions: solution pH – 6; ammonia to chlorine ratio 4:20, 5:25, 6:30, 7:35; AC dosage – 1 g and temperature - 25°C)

4.4 Characterization of fresh and exhausted activated carbon

4.4.1 Fourier-transform infrared spectroscopy analysis

Figure 4.21 shows the FTIR (Fourier-transform infrared spectroscopy) spectra of activated carbon before treatment, after treatment with synthetic solution, after treatment with brine solution. It can be seen that all of spectra are similar.

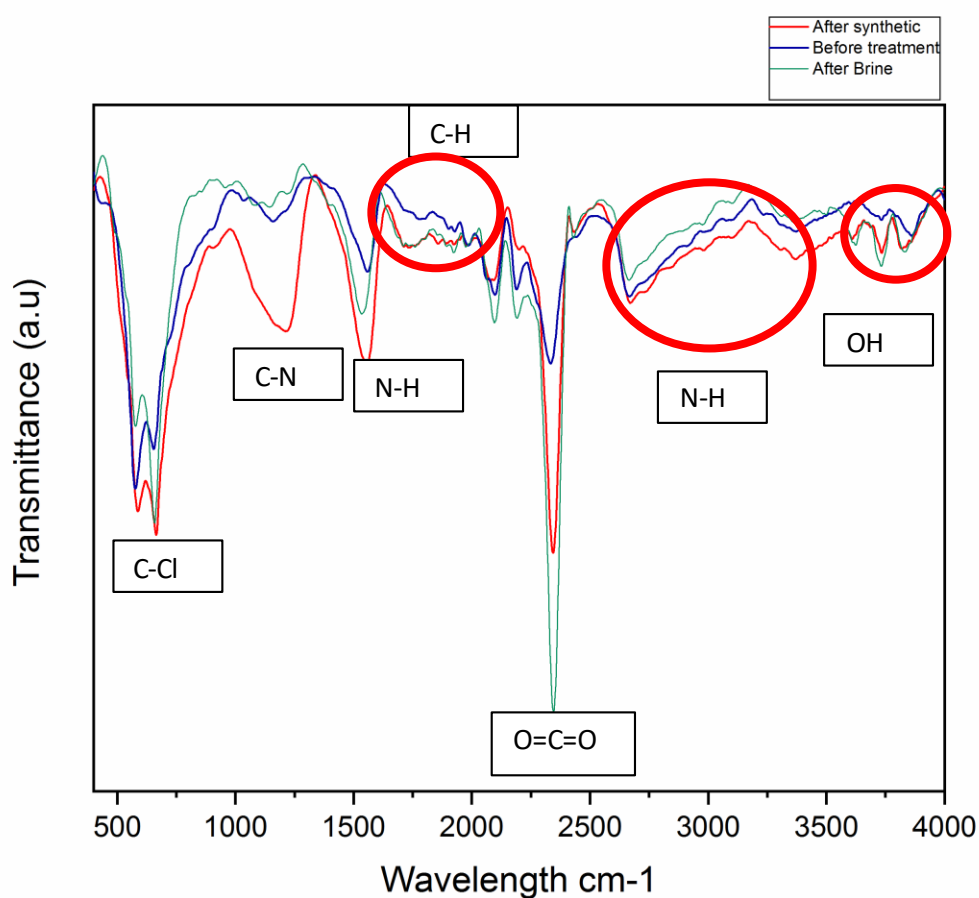


Figure 4.21 FTIR analysis of activated carbon structure

Strong band at 600 cm⁻¹, 700 cm⁻¹ and 900 cm⁻¹ are associated with C-Cl group. The peak at 1250 cm⁻¹ corresponds to C-N stretching vibration of amino group. Furthermore, a medium peak

at 1550 cm^{-1} of N-H bending amine compounds. Both peaks at 1250 cm^{-1} and 1550 cm^{-1} indicate that amino-groups of chloramines were adsorbed by activated carbon, and the chlorine – amine bond was destroyed after treatment. All of spectra has shown in Table 4.5.

Table 4.5 FTIR analysis determination

Transmittance (a.u)	Components
600 cm^{-1} , 700 cm^{-1} , 900 cm^{-1}	C-Cl group
1250 cm^{-1}	C-N stretching vibration of amino group
1550 cm^{-1}	N-H bending amine compounds.
1750 cm^{-1} , 1950 cm^{-1}	C=O stretching.
2000 cm^{-1}	C-H bending of aromatic compounds.
2150 cm^{-1} , 2240 cm^{-1}	C=C bonds
2340 cm^{-1}	O=C=O
of 3000 cm^{-1} , 3125 cm^{-1}	amine salt with N-H stretching vibration
3350 cm^{-1}	N-H stretching vibrations in primary amine compounds
3380 cm^{-1} , 3380 cm^{-1}	N-H stretch. Vibrations in secondary amine compounds.
3750 cm^{-1} , 3875 cm^{-1}	hydroxyl group presence

The presence of chlorine compounds indicated peaks at 600 cm^{-1} , 700 cm^{-1} and 900 cm^{-1} . Peaks at 1750 cm^{-1} and 1950 cm^{-1} indicate about C=O stretching

Aromatic groups are likely formed at high temperatures over 500°C , however weak peak at 2000 cm^{-1} shows C-H bending of aromatic compounds. These could be formed by decomposition of C-H bonds to form more stable C=C bonds at 2150 cm^{-1} and 2240 cm^{-1} , and finally transformed to O=C=O stretching of carbon dioxide group at the strongest peak at 2340 cm^{-1} . Also, on the structure surface, there was presence of amine salt with N-H stretching vibration at peaks of 3000 cm^{-1} and 3125 cm^{-1} . Peak at 3350 cm^{-1} is associated with N-H stretching vibrations in primary amine compounds and 3380 cm^{-1} , and peak at 3380 cm^{-1} identify the presence of N-H stretching vibrations in secondary amine compounds.

Existence of different peaks representing the structure of both primary and secondary amine compounds confirm our hypothesis that mono- and dichloramine could react with each other to form additional amount of trichloramine during adsorption process. Peaks at 3750 cm^{-1} and 3875 cm^{-1} are attributed to hydroxyl group presence on the surface of activated carbon.

4.4.2 Brunauer-Emmett-Teller analysis

BET (Brunauer-Emmett-Teller) analysis was carried out for activated carbon before any treatment, after treatment of synthetic solution and after treatment of brine solution from ERCO Worldwide. For all samples, the pore size and pore volume are the same, however, for sample after brine treatment the micro pore volume is drastically decreased by almost two times, Table 4.6. This phenomenon may be due to clogging of pores due to the precipitation of solid insoluble deposits from the brine.

Table 4.6 Surface area and pore volume and size of activated carbon samples

Sample	BET Specific Surface Area (m ² /g)	Langmuir Specific Surface Area (m ² /g)	Pore volume, cm ³ /g	Micro pore volume	Pore size, nm
GAC before treatment	1093	1582	0.58	0.45	2.11
GAC after treatment with synthetic solution	1092	1577	0.57	0.45	2.11
GAC after treatment with brine	602	723	0.32	0.25	2.09

Also, this was evidence of solid deposits on carbon obtained from batch experiments. There was sufficient amount of solids clogging micro pores, which decreased chloramine adsorption.

In flow system, in spite of reducing the surface area by two times due to clogged micro pores, activated carbon absorbed chloramines from brine. Thus, adsorption of chloramines on activated carbons meant to be effective for chloramine removal.

4.4.3 X-Ray Diffraction analysis

XRD (X-Ray diffraction) analysis was performed for activated carbon before treatment, after treatment with synthetic solution and after treatment with brine, (Fig. 4.22). It shows graphite structure of carbon (peaks at $2\theta = 26.6^\circ$ and 44.5°). This structure is known as turbostratic, which created due to parallel orientation of carbon layer planes (Azargohar and Dalai, 2006). All the peaks are sharp, which also demonstrate that the structure of activated carbon is graphitic.

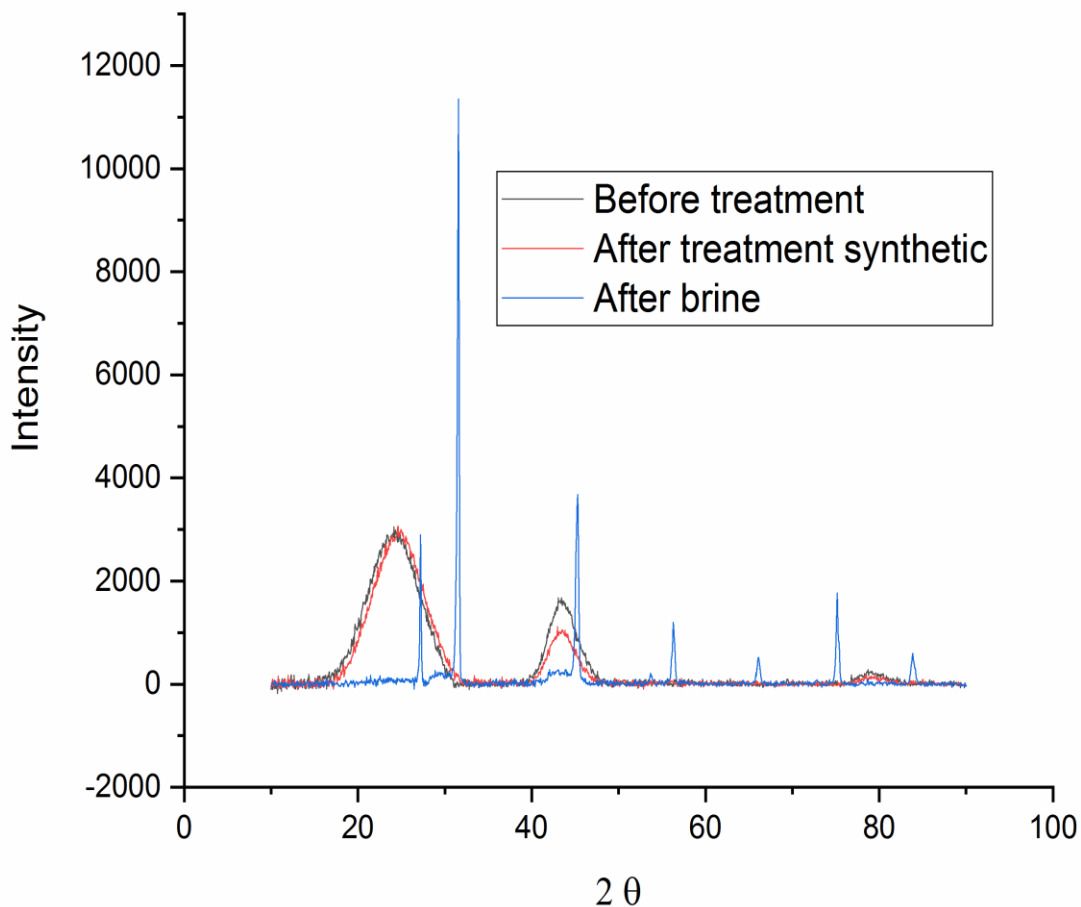


Figure 4.22 X-ray diffraction (XRD) of activated carbon before treatment, after treatment with synthetic solution and after treatment with brine

The brine solution originates from salt wells and the presence of other elements might affect the adsorption of chloramines on activated carbons. Peaks at 28° and 32° indicate presence of quartz (SiO_2) peak at 48 ° corresponds to metallic copper, peak at 58 ° represents a cristoballite (SiO_2), peak at 67° shows the formation of cobalt ferrite and peak at 85° indicates the presence of mullite ($\text{Al}_2\text{Si}_2\text{O}_3$).

4.4.4 X-Ray photoelectron spectroscopy analysis

XPS (X-Ray photoelectron spectroscopy) analysis was used to investigate structure of activated carbon before and after adsorption of chloramines from synthetic solution, Fig. 4.23.

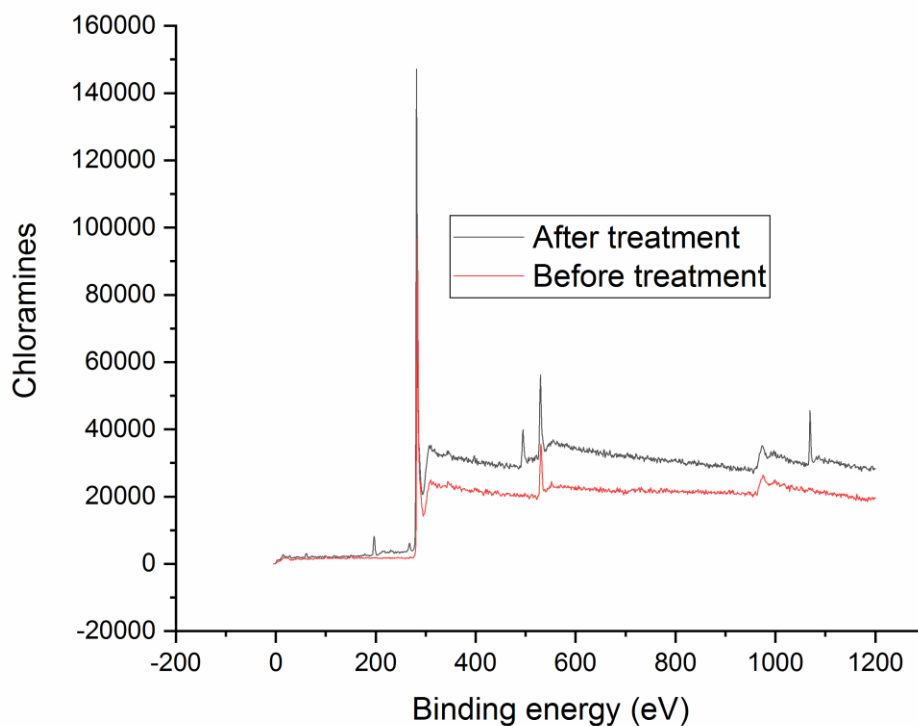


Figure 4.23 XPS analysis of activated carbon before and after treatment with synthetic solution

The XPS analysis shows presence of different elements on the surface of activated carbon which were adsorbed after treatment of synthetic solution. The results prove the high efficiency of adsorption on activated carbon for chloramine removal.

Peak at 200 eV corresponds to chlorine, 1000 eV indicates the fluorescence of oxygen, 600-400 eV – oxygen, 1200-1000 – sodium, and 200 -400 eV peak corresponds to carbon.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The optimum operational conditions were established for the removal of chloramines from synthetic and brine solutions using UV treatment and adsorption on activated carbons. Following conclusions were drawn from the study:

- The reaction between NaOCl and NH_4Cl leads to the formation of FC, MC, DC and TC and the fractions of FC, MC, DC and TC in reaction mixture is dependent on solution pH.
- UV treatment was found effective for chloramine removal from synthetic and brine solution. The maximum removal (100%) of chloramines (MC+DC+TC) from synthetic solution was achieved at pH 3, ammonia to chlorine ratio 1:5 in a reaction time of 30 minutes and at room temperature.
- Solution pH and reaction time are the key parameters affecting chloramine removal.
- Adsorption of chloramine by activated carbon from brine was found to be effective in a column study at these conditions: flow rate 6 mL/min, pH 6 and temperature of 25 ° C for 1g of activated carbon. 92% of trichloramine was removed by activated carbon in column studies.
- Investigation of structure of activated carbon by FTIR, BET, XRD and XPS confirmed the results of laboratory experiments that adsorption of chloramines on activated carbons is effective. Further usage of activated carbon and UV technology for chloramine removal from brine solution is recommended.

5.2 Recommendations

Both technologies, adsorption on activated carbons and UV radiation, are applicable for industry due to its effectiveness for high percent of chloramine removal. The UV technology requires the UV lamp usage which will increase the electricity consumption in plant. Also, it will require the new safety guidelines for whole plant due to high UV- radiation from UV-reaction. The availability of a power plant that provides electricity to existing caustic soda production should be consulted about potential additional introduced units of electricity consumption.

Usage of activated carbon should be performed in adsorption column in continues working mode as a set of two column, one of which is working and another is meant to be for activated carbon regeneration, otherwise the pores of activated carbon might be clogged by salt precipitation of brine. Activated carbon is unique adsorbent which can be regenerated by overheating at 600-900 °C. To produce the water vapor and obtain the desired temperature, the additional power is required. Thus, financial part plays a key role in making a decision which technology should be chosen.

All in all, both technologies are applicable and solves the problem. If 100% removal of chloramines is desired, UV technology is the best choice, if 92% of removal will be sufficient, the adsorption on activated carbons may be taken into account as well.

- Further usage of activated carbon and UV technology for chloramine removal from brine solution is recommended.
- Decreasing temperature of ERCO brine temperature to 30°C before implementation any of technologies do to it will decrease the initial concentration of chloramines is recommended.

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APPENDIX A

Calibration curve

Equation of calibration curve was used to adjust measurements taken on samples with unknown values.

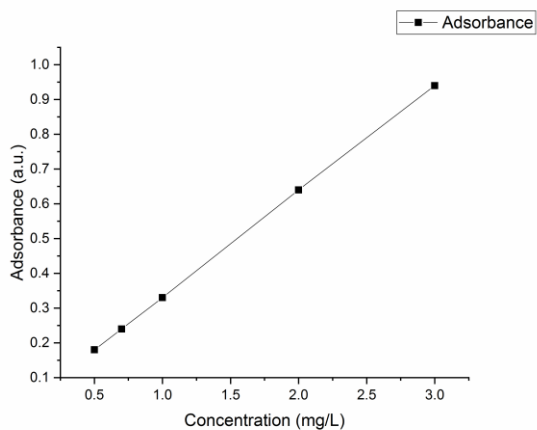
$$y = 0.302x + 0.037$$

Where y-absorbance, a.u.,

x- Concentration, mg/L

$r^2 = 0.997$, a statistical measure that represents the proportion of the variance for a dependent variable that's explained by an independent variable or variables in a regression model. (Wikipedia).

Concentration of chloramines, total, mg/L	Absorbance, a.u.
0.5	0.18
0.7	0.24
1	0.33
2	0.64
3	0.94



APPENDIX B

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